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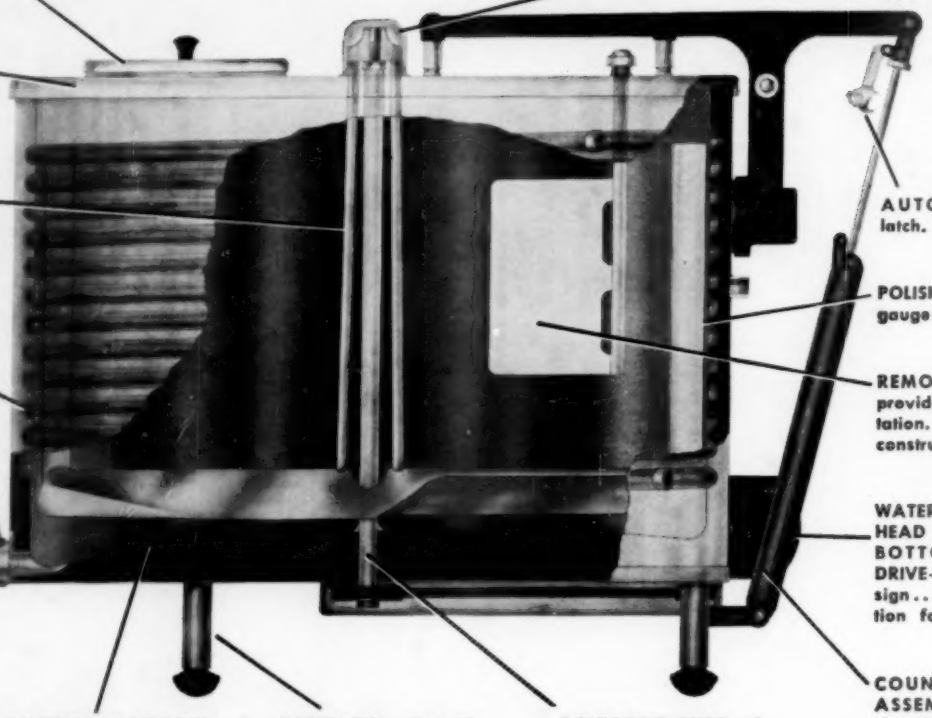

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Tin Plate for Food Containers

A Symposium

EDITOR'S NOTE: On June 18, 1951, a session entitled "Panel on tin plate for food containers," was held at the Eleventh Annual Meeting of the IFT. Berton S. Clark of the Research Department, American Can Co., Maywood, Illinois, presided. The four papers which constituted the formal presentation are printed here together with the record of the discussion which followed the formal presentation. John T. Knowles of Libby, McNeill and Libby of Chicago, Illinois, presided during the discussion.

This symposium presents an unusually clear and complete picture of the tin plate and can manufacturing industries in their relation to the food industries. It is for this reason that the papers are published here, together with the discussion which followed. The publication of this complete record of the symposium was made possible by the collaboration and financial assistance of the Can Manufacturers Institute, Inc.

Progress in the Tin Plate Industry[a]

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(Manuscript received July 17, 1951)

Progress in the tin plate industry in the past twenty years is reviewed. Changes in methods of processing and in the equipment used in tin plate manufacture are illustrated and described.

Tin plate manufacturing, like can making and canning, is big business. Last year the estimated volume of tin mill products reached a new peak and exceeded 5,300,000 tons or 7.5% of the total finished steel produced. The 5,300,000-ton figure is 500,000 tons above 1948, the previous high year, and double the tin mill tonnage rolled in 1929, the high year up until that time. To give a better conception of volume, it has been calculated that the tin mill products produced in 1950, if made into an uncovered cubical container, could hold all the water expected to flow over Niagara Falls in the next twenty-five years.

Because our customers continue to grow and because the tin plate industry continues to take full advantage of all new developments and technological advances, tin mill production can be expected to increase in the future. New capacity installed in 1950 should raise production in 1951, provided, of course, the world situation does not require limiting measures. In 1952 the production of two new plants will be available, one by Kaiser at Fontana, California, and one by the United States Steel Company at Morrisville, Pennsylvania. In addition, the output of many present plants will be increased.

Unlike the numerous plants of the can making and canning industries, there are only a few plants involved in the manufacture of tin plate. At the present time there are only twelve plants producing tin mill products in the United States. One glance at the tin mill of today reveals the reason: heavy and yet precision high speed machinery for mass production costing millions for initial installations.

The tin mill products *(4)* comprise a group of light-gage mild steel products falling in the general categories of (1) black plate, or plain uncoated sheets, (2) hot-dipped tin plate, (3) electrolytic tin plate, and (4) terne plate, or lead tin alloy coated plate. All products are manufactured in many hundreds of sizes varying by sixteenths of an inch, also in different thicknesses and chemical compositions, and several coating weights for the coated products *(5)*.

Where are these tin mill products consumed? It has been estimated that 75% of the tonnage used in the United States in 1949 was made into sanitary and general line cans. About 12% was exported. Crown caps and other closures accounted for about 5.5% of the total while 7.5% was fabricated into bakery and dairy tinware, gas meters, kitchenware, toys, signs, and numerous miscellaneous items.

Only two decades ago the first visions of a new process for rolling tin mill products appeared, the continuous hot and cold reduction of steel to tin mill gages and widths. A few years later, in 1937, a new tinning method was developed. The canning, can making, and tin plate industries analyzed both processes carefully and looked to the future. Today we look back at the complete revolution in processing and quality. It is the purpose of this paper to present briefly a picture of these twenty years of progress in the tin plate industry, with particular emphasis on the tinned product.

THE "WHAT" AND "WHY" OF TIN PLATE

Tin plate may be described simply as thin sheets of mild steel coated with tin, the steel sheets being in the neighborhood of 0.01 inch thick and the tin coating about 0.00006 inch thick. Many different thicknesses of steel are produced for tin plate and several coating weights are applied, but all are relatively thin as these typical figures reveal. Both the steel and the tin play their respective important parts in the successful use of tin plate. The steel, being roughly 75 to 400 times as thick as the tin, imparts the needed strength and rigidity, while the tin acts in a very unique way as the protective covering.

It is well known that practically all tin used in this country is imported from far off countries. This having been recognized, many extensive investigations have

[a] Presented at the Eleventh Annual Meeting of the IFT, New York, N. Y., June 18, 1951.

been carried on through the years for other metals or alloys to replace tin and tin plate. None have been found. Van Vleet *(12)* adequately summarized the situation in speaking before the American Society of Mechanical Engineers at New Orleans in 1948, when he stated that research on substitutes for tin have pointed to the conclusion that the only good substitute is less tin. The facts are that no other metal or alloy has met the essential requirements so well filled by tin plate. Why? Perhaps the best way to answer this question is to list some of the specific qualities and characteristics developed by tin and steel when combined into tin plate and fabricated into a container.

TIN PLATE QUALITIES AND CHARACTERISTICS

1. Corrosion resistance.
2. Low cost.
3. Ease of fabrication.
4. Light weight.
5. Strength and freedom from breakage.
6. Rapid and uniform heat transmission.
7. Lack of toxicity.
8. Ease of soldering at high speeds.
9. Ease of decoration.
10. Appealing lustre.

The fact that tin plate is still the only material which completely meets all requirements for food packing poses some special problems and difficulties, particularly in times such as the present. It does not mean, however, that the situation is hopeless. At such times we must overlook some of the ideal properties and fill the essential needs with black plate and tin plate of lighter coating weights.

The fact that we have had to resort to tin conservation on two occasions in one decade is accelerating investigations for tin substitutes. The studies are no longer restricted to a search for war time substitutes, but substitutes which may be more readily available during war or peace.

EARLY HISTORY

Although the art of coating iron with tin was known and practiced prior to 25 A.D., the first tin plate is reported to have been made in Bohemia shortly after the discovery of tin there in the year 1240 A.D. History records that the process was maintained a close secret until 1640, when the Duke of Saxony, through an agent, obtained enough information from Bohemia to enable him to begin the manufacture of tin plate. In 1660, Andrew Yarronton is supposed to have visited Saxony, returning to England in 1665 to establish production there. The manufacture of tin plate in the United States is relatively new, when compared with the early beginning of the industry in Europe. Although it is reported that tin plate was first produced about 1858 in a copper works at Pittsburgh, Pa. *(7)*, the industry in this country built its first firm foundation in the 1890's, about sixty years ago, as a result of the McKinley Protective Tariff.

By the time the industry got underway here, steel had been found superior to wrought iron, hot rolling had replaced hand hammering, and sulphuric acid, instead of barley water or vinegar, was being used to remove scale. Other improvements *(2)* prior to this time included the cold rolling of the pickled sheet to smooth the surface and improve the finish; the introduction of power-driven trimming shears and gas heated furnaces; the use of a flux in a compartment over the molten tin; and the tinning machine whereby the sheets were carried through the molten tin and oil by means of rolls.

In the early 1900's various mechanical devices and improved methods were introduced. At the time, these developments were of major significance and contributed materially to the progress of the industry. Many *(10)* of them, such as continuous heating furnaces for steel sheet bars, mechanical doublers, three-high mills for breaking down the pairs, and roller and catcher tables for the mills, resulted in either a better product or increased tonnage, oftentimes both. Without them the industry could not have met the increasing demands of the can making and canning industries for either quantity or quality.

A NEW PROCESS IS BORN

The complete revolution of manufacturing processes in the tin plate industry, however, is modern history. In fact, the cold reduction mill for steel of tin plate gages and widths is only twenty years old, just a youngster. The revolution has been amazing in respect to these new complicated processes and the short time in which it has been accomplished, even when considered in the light of this present technological age. Not only is it difficult to locate a single piece of equipment in any tin plate mill today which was in use only twenty years ago, but practically all machinery and equipment are totally different. Only the steel and the tin resemble their counterparts from the old tin mill. Even here the changes in processing appear to have changed the basic elements. In other words, the industry has been completely rebuilt from new foundations and on new principles.

THE REVOLUTION IN MANUFACTURING TIN PLATE

Home builders and building material people have effectively demonstrated their wares by picturing the old homestead "before", and "after". This suggests one means of displaying twenty years of progress in the tin plate industry. With the pictures, shown on the following pages, and some description, we can examine the two distinctly different processes; the "before", or "pack rolling", as it was called (Figures 1-6), and the "after", or the "continuous rolling" method (Figures 7-21) remembering that a very short time separates them. In fact, 70% of the tin plate produced in the United States in 1937 was "pack-rolled". In 1943, only six years later, the conversion was complete and the last "hot mill" for "pack rolling" was dismantled.

Although many fundamental operations have been conducted and much effort has been expended by the time the steel reaches the tin mill, only a bare mention can be made here of the actual steelmaking processes which impart such glamor to the steel industry. The iron ore, limestone, and coke are brought together from distant points, and charged into the top of mammoth blast furnaces to produce pig iron, which, in its molten state, flows from the bottom. Further refinement con-

tinues in the open hearth or Bessemer furnaces, which turn out a steel composition required by the tin mill. As we shall see later on, this composition has much to do with the final quality of the tin plate. This refined steel is poured into molds where it solidifies, and is then reheated to 1232° to 1260° C. (2250° to 2300° F.), and reduced to varying thicknesses before shipment to the tin plate producing plants.

THE OLD "PACK ROLLED" METHOD

Prior to the late twenties, the tin mills received the steel in the form of "tin bars", generally 8 inches wide, about 30 feet long, and approximately ½ inch thick. These bars were then cut to lengths corresponding to the width of the final tin plate, plus a certain allowance for side trimming of the hot rolled sheets. They were heated to about 732° C. (1350° F.) and "broken down" by rolling crosswise and singly, several passes through the "hot mill" being required (Figure 1). Two of these

FIGURE 1. Closeup of hot rolling on the roughing mill. Here hot "tin bars" were reduced, folded into packs, reheated and finally reduced to gage on a finishing mill of similar construction.

pieces, known as "breakdowns" were matched together and then the "doubles" were given two or three additional passes. The individual sheets were separated, then matched and doubled in squeezing or doubling machines to make a pack of "fours". The "fours" were reheated, rolled two or three passes, "opened" by separating individual sheets, matched, doubled to a pack of "eights" and trimmed on one end. These "eights" or "finish" packs were reheated and rolled several passes to a measured length. The gage or basis weight was determined by the weight or thickness of the original "tin bar" and the length to which the final pack was rolled. The packs were allowed to cool and then sheared to the ordered size. The pack having been sheared to size was then "opened" (Figure 2). This hot rolled plate, termed black plate, was freed of scale or oxide by "black pickling" with sulphuric acid (Figure 3) then stacked in piles and softened by "black annealing" at about 760° C. (1400° F.) (Figure 4).

During the several hot rolling steps there was always a tendency for the sheets to weld together. This tendency was lessened considerably by using a steel containing specified but fractional percentages of phosphorus and silicon, the two elements which, we shall see later, lowered the corrosion resistance of tin plate under certain conditions.

Heating the plate, as is accomplished in "black annealing," referred to above, caused recrystallization of the internal structure of the steel which had been severely distorted during hot rolling, removed the hydrogen absorbed during the pickling, and cleared the surface of water and ferrous sulphate. For most purposes the "black annealed" plate was too soft and had unsuitable forming characteristics and too rough surface. In order

FIGURE 2. Shearing and opening hot-rolled packs. The plate was usually hot "pack-rolled" in multiples of 2 or 3 lengths and the finished packs contained 8 sheets. After shearing into pattern sheets, the sheets were opened or separated by hand.

FIGURE 3. Black pickling. After the sheets were separated, they were placed in racks and immersed in acid to remove the iron oxide developed during hot rolling.

FIGURE 4. Annealing furnace. The stationary furnaces were charged with 3 or 4 individual pots or boxes and the furnaces were heated to about 1400° F. The heating cycle averaged about 20 hours.

to improve it in these respects, the "black pickled and annealed" plate was given a certain amount of cold rolling to stiffen it, flatten it, and produce a smoother surface (Figure 5). However, the cold rolling required to produce the desired smoothness was usually sufficiently severe that a second annealing at about 538° C. (1000° F.), "white annealing," was generally practiced. These annealing treatments introduced some surface oxidation which was removed by another pickling operation known as "white pickling" (similar to Figure 3). Following this final pickling, the plate was washed and placed in boshes filled with acidified water and held for hot dip tinning which is described in a later section (Figure 6).

FIGURE 5. Three stand tandem two high cold rolls. After annealing the black plate was cold rolled on a 3 stand tandem two high mill. This operation imparted a bright surface, tempered the plate and improved the flatness.

FIGURE 6. Tinning. Black plate was removed from boshes and fed by hand into the tin pot, two or three sheets abreast. The sheets entered the flux, were carried through the molten tin and then passed up through the tinning machine which was immersed in palm oil. After emerging from the oil the tinned sheets were run through a branning machine to remove the excess oil.

THE NEW "CONTINUOUS ROLLING" METHOD

Although many mechanical developments in the "pack rolling" process, mentioned previously, were directly instrumental in improving tin plate quality and costs, they were not sufficient to compete with the wide continuous strip mills which were developed for the thin tin plate gages between the years 1925 and 1930. Continuous hot rolling and subsequent cold reduction of strip were practiced many years before, but always in the narrow widths. In November, 1927, the first continuous hot strip mill for tin plate "breakdowns" was started at the Gary Sheet and Tin Mill of the American Sheet and Tin Plate Company, now United States Steel Company. Instead of small "tin bars" this mill permitted the use of slabs weighing about 2000 pounds which were rolled hot in a train of mills to 16 or 18 gage (0.062-0.050 inch). This long strip was then cut into short lengths to form "breakdowns" similar to those which were obtained from the "tin bar". From this point, the subsequent treatment for production of black plate was similar to that already described.

In 1929 another milestone in continuous rolling was reached when the Wheeling Steel Company produced the first commercial cold-reduced tin plate. This "cold reduction" process consisted of starting with strip from the new type hot-strip mills, just described, and reducing it to tin mill gages while "cold" rather than "hot".

As we look back, it is now apparent that many revolutionary technological advances in several individual fields were required to bring about the development of the wide strip mills for thin-gage strip, with all branches of science contributing in a major way. Four-high mills, consisting of two work rolls, through which the strip passes, and two larger backup rolls for support, were a necessity now well recognized. Developments in the electrical engineering field pertaining to electrical controls, gages and meters, were essential. Roller bearings, lubricants and lubrication methods also share in a big way in the accomplishment *(1)*.

As continuous methods for production of tin mill products were expanded, treatments which, through constant research and development, were found to improve quality have been installed as a part of an already established operation. In other words, some original fundamental operations have developed into series of operations. Furthermore, the continuous operation, along with the technical skills of the chemists, physicists, metallurgists, and engineers has brought about a degree of control over the operations which was not previously known or possible. Controlled quality and all the obvious benefits have resulted.

To bring out the individual steps in each fundamental operation, their part played in producing quality tin plate today and the control exercised over them, the following details will be of interest.

Slab conditioning and the hot-strip mill. Most tin mills of today begin the conversion into tin plate with steel slabs received from the steel production units (Figure 7). The slabs measure approximately 30 inches wide by 7½ inches thick, are generally more than 200 inches long and weigh about 14,000 pounds. After the removal of surface defects, which might interfere with subsequent high-speed operations or result in defective finished tin plate, the slabs are heated to 1204.5° C. (2200° F.) and then reduced to about 0.080 inch on the continuous hot-strip mills. As shown in Figures 8 and 9, the operations may consist of ten 4-high mills in tandem. These mills, as is necessary with all tandem mills, are electrically synchronized so that each succeeding mill operates at a greater predetermined speed than the previous mill. For example, if the fifth stand operates at 250 feet per minute, the tenth stand must operate at 2000 feet per minute at normal reduction rates. Careful pyrometric control is essential as the strip emerges from the last

FIGURE 7. Slab conditioning. All slabs are hot scarfed on the edges with the top and bottom surfaces being spot scarfed to remove defective areas prior to hot rolling.

FIGURE 8. Hot strip mill: Finishing mills and sprays. After passing through the roughing stands, the semi-finished strip is rolled through 6 closely coupled 4-high mills to an average thickness of 0.080 inch following which the hot band is subjected to heavy water sprays for cooling.

stand and also as it is coiled because properties established during this early operation affect the properties of the finished material.

Continuous pickling and cold reduction. Scale which is formed during hot rolling is removed by pickling in sulphuric acid to obtain a clean steel surface (Figure 10). Oil is then applied to protect this clean surface from rusting and scratching and to assist in cold reduction which follows (Figure 11). The final gage of the tin plate is determined in the cold reduction operation which consists of either four or five stands of four-high mills in tandem. The cold reduction, amounting to about 90%, has lengthened the strip to as much as two or three miles, depending upon the original weight of the hot strip coil and the finished gage. This terrific cold compression, with attendant elongation, necessitates a lubricant and coolant which generally consists of palm oil or a mixture of oil and water. As with all the fundamental operations, many improvements have been made in the cold reduction mills since the early ones. Electrical controls are now far superior and speeds have increased tremendously. New mills are reported to be operating at close to a mile a minute in contrast to speeds of one-fourth that rate just a short time ago. All mills are equipped with a "flying micrometer" at the exit end which permits the roller to regulate the final gage thickness.

FIGURE 9. Hot strip mill: Coiling. Starting with a slab 17 feet long, the finished hot strip is extended to about 1350 feet in length and coiled.

FIGURE 10. Continuous pickling unit. The hot-rolled coils are pickled by immersion in 4 acid tanks, rinsed and oiled.

FIGURE 11. Five stand tandem cold reduction mill. The pickled hot-rolled coils are reduced from 0.080 to 0.010 inch in one pass through the five stand tandem cold reduction mill. An oil emulsion is sprayed on the mills. It acts as a lubricant, and as a coolant to remove part of the heat which develops during cold reduction.

Cleaning and annealing. Oil, clinging to the strip as it is coiled at the exit end of the cold reduction mill, is removed in a continuous alkaline cleaner (Figure 12). Otherwise, the oil would be burned during annealing, leaving a residue on the surface which would prevent good tinning.

The cold-reduced strip is extremely stiff and very low in ductility. Therefore, a heat treatment is necessary (Figure 13).

FIGURE 12. Cleaning lines. It is necessary to remove the oil from cold reduced coils by alkaline cleaning prior to annealing since charred oil would burn into the strip surface and interfere with tinning operations.

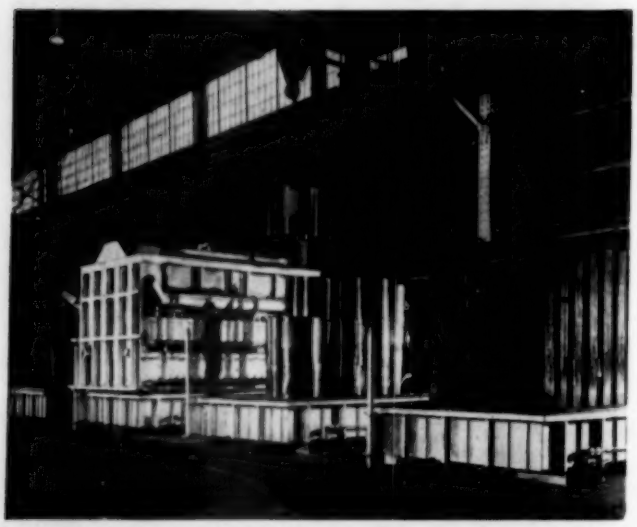

FIGURE 13. Annealing. Coils are heated to approximately 1200° F. to remove the strain developed in cold reduction. The annealing is done in a reducing atmosphere to prevent development of surface oxidation during the cooling operation.

The importance of close control over the annealing temperatures has been recognized for many years because this treatment regulates, to a large extent, the final physical characteristics. Recent studies are stressing the part played by this operation in determining the corrosion properties as well. These findings are bringing about revisions of annealing practices throughout the industry.

The operation is conducted at about 949° C. (1200° F.). An atmosphere, designed especially to hold the bright surface and produce a quality product is maintained in the annealing chamber throughout the heating cycle and most of the cooling cycle.

Temper rolling. The story of the development of tempers and the equipment required to obtain them is contained in a later section entitled "Physical Characteristics". The modern temper mill, however, must impart the proper shape to the steel strip and also the desired surface finish, as well as the hardness or temper.

The operation shown in Figure 14 consists of an uncoiler, two heavy 4-high mills, similar to those of the cold reduction mill, and tension rolls in front of the coilers. Reduction and stretching work together to obtain the temper and flatness.

To produce the harder grades of tin plate the "work rolls" in the first stand are often shot blasted. The rough finish, imparted to the strip by these rolls, permits the smooth surface of the "work rolls" in the second stand to get a better grip on the strip. This, in turn, permits additional cold working required to meet the higher temper. Hardness checks are made after the first rolling. Oftentimes a second pass is needed to bring the strip into the desired temper ranges.

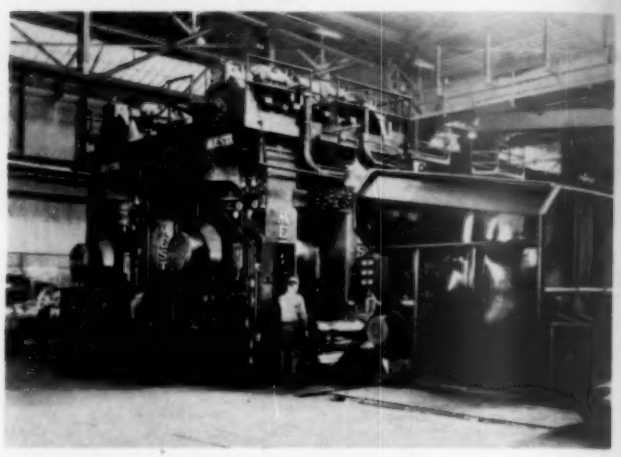

FIGURE 14. Two stand tandem temper mill. Temper rolling is one of the key steps in the manufacture of tin plate. In this operation the final base surface finish, temper and flatness are obtained.

For the majority of tinned products, a bright surface is required and so smooth rolls are used in the second stand. However, various surface textures are made, particularly for electrolytic tin plate and black plate, by different temper roll finishes.

Continuous shears, pickling. For hot dipped tin plate and for black plate the next operation is shearing. Coils for electrolytic tin plate are not sheared because the tinning process is done in strip form. The shearing operation of today includes several important steps, each having a bearing on the final quality (Figure 15). After uncoiling, the edges are trimmed to one of the finished dimensions. The strip is then scanned by an electric-eye to detect holes which may have been made accidentally in the steel base during the previous rolling operations. Next, the strip passes through a "flying micrometer" which detects sections, if any, which are outside commercial weight limits. Both the electric-eye hole detector and the micrometer are synchronized with the shearing so that the portion of the strip containing holes or off-gage material is later automatically deflected into discard pilers. A roller leveller operation follows to remove coil set before the actual shearing takes place. The sheared plate is then carried away by conveyors to pilers.

The sheared plate which is intended for hot dip tinning is pickled in hot dilute sulphuric acid. Although the surface of cold-reduced plate annealed by present-day practice usually is free of noticeable iron oxide, some pickling is necessary to prepare the surface for tinning. Pickling is generally accomplished with equipment similar to that shown in Figure 3, but the latest development of electrolytic pickling attached to the entrance end of the tin stack is now becoming standard practice in many plants. This is described more fully under "Research Continues".

Hot-dip tinning. The vital tinning operation, which adds so importantly to the value of the steel, is accomplished by two specific and radically different methods, hot dipping and electrolytic tinning. Hot-dip tinning and all the many problems involved have been completely described by Crombie *(4)*. Inasmuch as this paper is quite recent and also since a companion paper in this series *(9)* covers this subject, bare mention

FIGURE 15. Shear lines. The temper-rolled coils are side trimmed and sheared to finished size for hot-dipped tin plate and black plate. Each unit is equipped with a pinhole detector and gage selector.

of this operation is made here to complete our sequence of fundamental operations in the production of hot-dipped tin plate. Electrolytic tinning, being a major new development of the tin plate industry, is reviewed in detail under a heading "Electrolytic Tin Plate".

Although the basic principles and the art of hot-dip tinning have remained essentially the same for many years, the past twenty-five years have produced one development after another until the modern tinhouse has little resemblance to its earlier counterpart. The tin pot has been mechanized to a high degree, hand feeding has been eliminated, present day roll and brush designs are superior, heating systems have been improved, pyrometric control has been installed in the tin and oil baths, and a better method of cleaning has been devised *(15)*.

The major steps in the operation of tinning the plates are fluxing, tinning, and removing excess oil (Figure 16). Driven rolls carry the sheets through the zinc chloride flux and into the molten tin, then through three sets of rolls which are immersed in palm oil. These rolls are known as the tinning machine and their purpose is to squeeze the excess tin from the sheets as well as to control the tin coating weight and distribution. The molten tin is usually at a temperature of about 329.5 to 342° C. (625 to 650° F.) while the palm oil is controlled close to 240.5° C. (465° F.). The palm oil has the two-fold purpose of keeping the molten tin free from oxidation and of reducing the temperature of the molten tin on the sheets to slightly above the melting point [232° C. (450° F.)] before exposure to the atmosphere. After emerging from the tinning machine, the tin coating is solidified by an air blast. In most tinning units the palm oil carried on the surfaces of the plate is partially removed in a very dilute soda-ash solution, the plate is rinsed and then goes through a "branning" machine for final cleaning and distribution of the oil film. In most present day installations the finished hot-dipped tin plate is then hand assorted and packaged for shipment as shown in Figure 17.

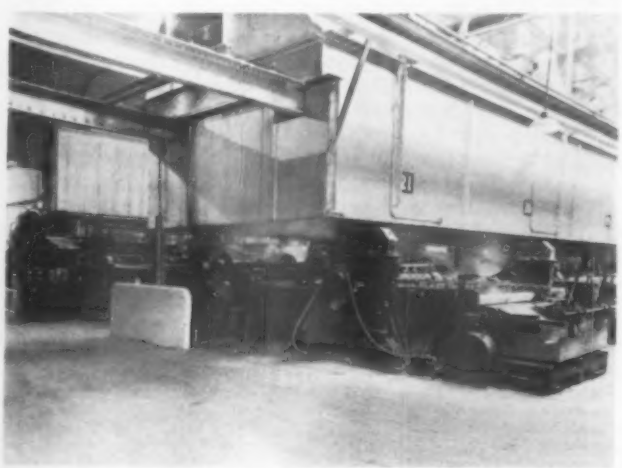

FIGURE 16. Tin stack: exit of unit. After tinning, the plate is passed through an alkaline washer to remove most of the palm oil and then passes through a branner to remove additional oil. The plate is then piled automatically and conveyed to assorting room for final inspection.

FIGURE 17. Assorting room. General view of present day assorting room where hot-dipped tin plate is assorted, counted, weighed and packaged for shipment.

IMPROVED QUALITY

Progress in the tin plate industry in the past twenty years has by no means been confined to equipment. New production processes, new methods, new treatments and quality control procedures have raised the over-all quality to levels which were beyond the imagination only a few years ago. The steel itself is far superior and several grades are available to help regulate final properties of the tin plate; present day corrosion resistance takes away much of the risk of packing the so-called "most corrosive" food products and allows use of lighter coating weights at considerable savings; physical characteristics are significantly better and methods have been established for controlling tempers within reasonable limits; the improvement in surface uniformity and the reduction of glaring surface defects have been outstanding; and the standards for gage, flatness, and shearing are far beyond those previously obtained. Further consideration is given to these improvements in the following paragraphs.

The steel. In 1930, when the author first became interested in tin plate and tin cans, and, for some years thereafter, two grades of base metal were available for our use, Bessemer and open hearth. The names denoted the type of furnace in which the steel was produced. Bessemer steel was harder and stiffer and was generally used for large diameter cans, while the somewhat softer open hearth steel was considered best for cans of small diameters. The two distinct characteristics existed because of the nature of the steelmaking methods, inasmuch as the type of Bessmer converters used in this country at that time

turned out a steel higher in phosphorus and nitrogen, both hardening agents, than was contained in the tin plate steel from the open hearth. At that time, many different grades of steel were produced for the other types of steel products, but the hot "pack rolling" required the presence of certain elements, such as phosphorus and silicon, for economical production. In fact, the sheets were welded together during the rolling operation unless the steel contained some phosphorus. The "cold reduction" process has actually resulted in a new era in respect to composition of steel for tin plate and, as a result, a specific steel chemical analysis is ordered from the steel producing plants for each type of tin plate made today. The metallurgical control begins with the iron ore, coal, limestone, and steel scrap, for these basic materials are known to influence in a significant manner the can making operations and the service life of the finished containers. It is not unusual to find 15 or 20 steel grades in the tin mill of today. Certain of these are specified by the can maker to meet corrosion or physical requirements while other steel grades are required by the producing plant to meet other quality considerations. The wide variety of steel compositions permitted by the cold reduction process has resulted in tailor-made tin plate. As an example of this, consider the No. 2 can. Tin plate from any one mill may be produced from ten or more steel grades, the chemical composition depending upon the mill equipment, the can maker's machinery, and the product to be packed in the finished container. True, the composition of one grade is not always greatly different from another, but in many instances even small differences are significant. This will be demonstrated in the following paragraphs in connection with a discussion of corrosion resistance and physical characteristics.

Corrosion, hot-dipped tin plate. All those who have had experience with the canning of the "most corrosive" products, such as colored fruits, are familiar with the strides which have been made by the tin plate and can making industries in increasing corrosion resistance of tin plate containers. The progress has been truly significant. Hartwell *(5)* has given an excellent review of this phase of the subject, but some mention of this development will be of interest here.

For the past twenty years, no other quality problem in the tin plate industry has been given more attention. Although prior to 1930 considerable research work in connection with the theory of internal corrosion, the effect of tin coating weights and the effect of the steel itself was carried on, early progress was impeded because the method of producing tin plate required a specific steel composition, at least in respect to those elements which were found later to play so important a part in the corrosion of tin plate containers. Serious hydrogen swell losses with fruits in California in 1930 markedly accelerated the investigation of the corrosion problem, including the study of cold-reduced tin plate. The cold-reduced product was far superior—simply, as was later determined, because of the steel composition which could best be used by this new process. Major developments followed and investigations leading in many directions have continued on a large scale since that time.

The corrosion problem has been most complicated and, at times, very confusing. The complexity arises from many factors, including packing and storage conditions. In addition, each food product differs in its reactivity with the container, be it a tin can or a glass jar with metal closure. In fact, large variations may exist between different lots of the same product because of variations in growing conditions, maturity, and the like. Furthermore, completely different corrosion conditions generally exist with a particular food product depending upon whether the can is plain or enameled. However, regardless of the many factors, other than tin plate, contributing to corrosion, the effect of steel composition has been gradually unwoven.

The effect of each element contained in mild steel has been systematically studied. Thousands of experimental lots of tin plate and thousands of experimental food packs by can makers and canners were required. The effect of silicon in the steel was the first to be established. This element was added to steel in small amounts (0.03 to 0.08%) to minimize sticking in "pack rolling". Until the extensive hydrogen swell losses, in 1929 and 1930, the industry was not aware of its detrimental effect on corrosion. Investigations then and since have revealed that silicon has a greater effect on the corrosion in plain cans than any other element. The varying reaction, depending upon whether the container was enameled or plain, was demonstrated here in that silicon did not have this drastic effect in enameled cans. Expensive annealing treatments were found to minimize the effect of silicon in plain cans, but the cold reduction process permitting extremely low silicon steel was the economic answer. All tin plate steels today are extremely low in silicon, usually under 0.01%.

The part played by phosphorus, another element required to the extent of about 0.08% for the pack rolled process, was also settled with the advent of cold reduction. Here was an element which showed its detrimental effect mostly in the enameled can and with the "most corrosive" products, such as the colored fruits, pureed products, sauerkraut, beets, and pickles. Today, only the minimum possible phosphorus content steel, usually under 0.015%, is used for containers for these products. This extremely low limit for phosphorus, however, has not been found to be required for the "mildly corrosive" or the so-called "noncorrosive" products. Many experimental packs with selected products from these classes have shown no difference in corrosion resistance between low phosphorus and high phosphorus steels.

Carbon, manganese, and sulphur, in the amounts required in steels for the cold-reduced product, fortunately, appear to have no significant effect on corrosion. Many experiments with other elements, such as copper, nickel, chromium, molybdenum, and perhaps others, have revealed some lowering of resistance to corrosion with the "most corrosive" products, but this is not shown with the "mildly corrosive" or "noncorrosive" products.

As a result of the many investigations, chemical specifications for tin plate have been established and now longer shelf life for practically all products is assured, ranging from thirty to several hundred percent greater than was previously possible. Examples of improved shelf life are shown in Table 1, prepared by Clark and Brighton *(3)*. The data for 1931 antedate the development of cold-reduced plate, while those for 1944 show the improvement from the use of the cold reduction process and

TABLE 1

Shelf life of canned fruits and vegetables. Central United States [21° C. (70° F.)]

Products	Tests reported in	
	1931 [b]	1944 [c]
	Shelf life in months	
Apples and Applesauce	12-15	36
Apricots	18-24	36
Blackberries	9	12 or more
Blueberries	12	12 or more
Cherries, R.S.P.	9	12 or more
Cherries, sweet	12	12 or more
Cherries, black	9	12 or more
Cranberry sauce	12	12 or more
Fruit salad	9-12	36
Grapes	9	12 or more
Grapefruit	9	36
Peaches	18-24	36
Pears	24	36
Pineapple	12-15	36
Plums	9	12 or more
Rhubarb	6	12 or more
Asparagus	24	36 or more
Beans, Lima	24 or more	96 or more
Beans, stringless	24	36 or more
Beets	15	48 or more
Brussels sprouts, cabbage and cauliflower	18	48 or more
Carrots	24 or more	36 or more
Corn	36-60	96 or more
Hominy	36-60	96 or more
Peas	36-60	96 or more
Pickles	6	12 or more
Pumpkin and squash	18	48 or more
Sauerkraut	9	12 or more
Spinach	18	36 or more
Sweet potatoes	24	48 or more
Tomtoes	15	48 or more

[b] *Fundamentals of Canning and Canned Fruits and Vegetables.* Bulletin No. 5, Series X. The Quartermaster Corps Subsistence School, 1931.

[c] *Fundamentals of Canning,* Test No. 23 Tentative, Quartermaster Subsistence School, 1944.

accompanying changes in steel composition. These authors who have spent much of their time in this development also go on to point out the possibility that shelf life is actually greater than illustrated. In other words, the "or more" in the table is significant.

Even since 1944, research has uncovered other important factors having a bearing on service life of the "most corrosive" products. For years their effect was shadowed by the effect of steel composition. Having removed these shadows, the other factors began to appear. The effect of each tin plate processing step has been systematically investigated. Vaurio *(13)* has demonstrated that, with prunes, at least, the more corrosion resistant the steel, the more effective is the cathodic protection of the tin. Gradually knowledge of the differences in the corrosion resistance of the steel to which he refers, is becoming available. It is known that the surface prepared for tinning is important and that annealing and annealing atmospheres, for example, play a significant part. There are, however, still many aspects to be considered further and today as much or more attention is being given the corrosion problem than at any time previously. One thing is clear: still further advances in corrosion resistance will be made in the future.

Physical characteristics. The first cold-reduced plate inherently had an outstanding physical characteristic which was immediately recognized: superior drawing properties. This improvement may have seemed more important to industries which make much use of deep stamping operations, but it was also significant to the container manufacturer. The "pack-rolled" product was limited in respect to deep drawing. A heat treatment, known as normalizing, had been developed and the normalized "pack-rolled" product was fairly satisfactory but at an increased cost. Today, the drawn products made from cold-reduced steel are far superior to those made in the past with the normalized "pack-rolled" product. True, the steel is also superior today but much credit must go to cold reduction and the new processing treatments.

Other physical requirements, such as resistance to paneling, buckling, denting, and fluting, were not met with the first cold-reduced plate, nor for some time later.

Early trials of the cold-reduced product for sanitary cans revealed these weaknesses. It could not be used for end stock on the larger cans, nor for bodies of containers in which a good vacuum was necessary without resorting to the heavier tin plate weights which added considerably to the cost. This limited its use to the small cans. Even with the smaller cans, denting was serious. In other words, the plate simply was too soft. For quite some time this condition limited the general adoption of the process by the industry.

Like the corrosion problem, the temper problem involved years of research by the tin plate and container manufacturers. Consideration was given to each fundamental operation to determine the part it might play. It was known that steel composition could be changed to produce harder tin plate but this increased the rate of corrosion with many highly corrosive products and, therefore, could not be tolerated. Lower annealing temperatures were also effective to some extent, but, again, corrosion resistance was impaired. Finally, 4-high cold rolling after annealing was adopted as a safe means of obtaining greater stiffness.

Continuous cold rolling equipment, similar to an individual stand of the cold reduction mill, then replaced the 2-high cold rolls which had been used for the "pack rolled" product and the operation became known as temper rolling. Even with this heavy equipment the hardness required for certain cans, particularly the larger ones, could not be met. Subsequently, two heavy stands, involving a large expense not originally anticipated, were placed in tandem and a serviceable product was then available.

By this time the corrosion studies had revealed that phosphorus and other steel-hardening agents did not reduce shelf-life of the "non-corrosive" or "mildly corrosive" food products. Therefore, these hardening agents could be added to the steel for many requirements. Today, the steel chemical composition, steel treatment, and temper mills work together to produce the hardest grades. It is now known that these grades resist buckling, paneling, and denting to a greater degree than was possible with tin plate made by the "pack-rolled" method.

While the tin plate industry was searching for a means of producing harder cold-reduced plate, the proper temper for the various sizes and types of containers was being developed by the can making industry *(12)*. Based on the results of these studies and the development of means of obtaining temper, a "Temper Classification", now quite well established in the industry, was set up. As Clark and Brighton *(3)* put it, "This made it possible to fit cans to the intended use both from the standpoint of the corrosion potentialities of the product to be packed and from the physical abuse which the can had to withstand."

Surface. The improvement in surface uniformity and the reduction of glaring surface defects, so prominent with "pack-rolled" plate, too often has been overlooked in analyzing the progress in the past twenty years. However, anyone close to the production or use of tin plate through the years recognizes a vast improvement which has had its effect in making better cans with greater lustre.

Another progressive step in regard to surface conditioning has been taken with cold-reduced plate. It pertains to the type of finish as explained in more detail in other sections. Several different surface finishes are obtained at the temper mills, the desires of the consumer determining the type for any particular use.

Shape, shearing, and gage. Flatness, shearing, and gage accuracy are three plate characteristics important to the can making operator. They may not be obvious to the casual observer, but are a necessity with present-day speed. The high-speed enameling, lithographing, and can line operations would not be possible with the standards of past years.

As has been mentioned earlier, the temper mill both by reduction and stretching, is generally considered the critical operation for obtaining flatness, and yet other operations play very important parts. The shape of the strip as it comes from previous hot and cold reduction operations is a major factor. Knowledge of these factors which has been accumulated over a period of years has contributed much toward development of practices capable of producing flat plate.

ELECTROLYTIC TIN PLATE

The success of continuous methods for rolling thin strip in widths required for tin mill products led to consideration of continuous hot-dip tinning. Many efforts were made, finally attaining some success with narrow material but leaving unsolved many problems with strip of tin mill widths. Furthermore, it was soon realized that the auxiliary equipment required for a continuous line would be so extensive that greater speeds than appeared possible would be required if the operation were to be economically sound. About this time the "general line" type of containers for packaging the many miscellaneous products which are so popular today were being adopted on a large scale. It was evident that many such containers would not necessarily need the tin coating thicknesses required for many "sanitary" cans. Efforts to produce the very light hot-dipped coatings either continuously or by individual sheets, were not satisfactory. These several conditions, plus the need for a cheaper product, were the responsible factors resulting in the initiation of development work on electrolytic tin plate.

Like with most major technological developments, a book could be written of the research work carried on by many companies within the tin plate and allied industries prior to the first commercial electrolytic plating installations. The Carnegie-Illinois Steel Company's (now United States Steel Company) development went beyond the research laboratory stage in 1937 when the

first commercial installation was made at the Gary Sheet and Tin Mill. This line for full size electrolytic tin plate production was designed to operate at 150 feet per minute and produce an unmelted, scratch brush finished coating of 0.50 pound per base box,[d] a saving of 1.00 pound over standard coke hot-dipped plate.

Extensive investigations were conducted with this early product to develop uses. Most attention was given to the "general line" field where lighter tin coating weights were thought to be more practical. Fortunately, the can makers' technologists had included some experimental wet food pack tests in their studies of the first commercial electrolytic tin plate, and these data formed the first guidepost for promulgating the feasibility of the wider use of lightly-coated tin plate during the second World War. In the early part of the war, the Government considered restricting the use of tin plate to the armed forces and "Lend-Lease" only, eliminating it entirely for civilian consumption. This was avoided only by the cooperation of all concerned in the conservation of tin. This tin conservation brought about an expansion of the electrolytic tinning process and new lines were installed by the steel industry in the early forties. Lines for bonderizing black plate were installed at the same time, permitting production of a chemically treated product which, when enameled, also contributed in a major way to the tin conservation program.

The very first electrolytic tin plate left much to be desired. It is not difficult to recall the early product. At times, the tin coating flaked during stamping operations, it discolored readily, would not lithograph, much of it had poor enamel adhesion, also poor solderability, and the corrosion resistance was questioned. The apparent economy, however, forced solution of these perplexing problems. Each year since development work was undertaken, research budgets have contained large sums for improvement of the product. Specific details of the investigations and developments are too lengthy for discussion here, but at least attention should be called to the improved electrolytes, the development of melting processes for the tin coating, new chemical treatments for better enamel adhesion, and new oiling processes. All of them were major accomplishments. The quality has now been improved to the point that electrolytic tin plate is firmly established. In 1950, electrolytic plate production amounted to about 60% of the total tinned product.

Three types of electrolytic processes are in use in the United States. They are often referred to according to the types of electrolyte which has been adapted to them: sulphonic acid, halogen, and alkaline. All processes embody a number of operations in tandem, many of which have been added since the first line started in 1937. Briefly, the type of modern lines shown in Figures 18 and 19 contain heavy uncoilers; automatic welders for joining coils; looping pits or towers for accumulation of excess strip permitting continuous operation while coils are being welded together; electrolytic alkaline cleaning and electrolytic acid pickling for preparing a clean surface for the tinning which immediately follows; then the electrical resistance tin melting operation, and water quench for the solidification of molten tin; an electrolytic chromate chemical treatment for obtaining resistance to discoloration and imparting better adhesion of organic enamels; application of a light oil film to minimize oxidation of the tin and to serve as a lubricant; roller leveling to remove coil set and improve flatness; shearing; inspection; and piling. Rinsing and drying operations are also included between tanks used for the various wet operations. Each line is equipped with gage and hole detectors, as well as automatic accessories to discard off-gage material, plate with holes, and other defects which investigations and experience have indicated may render the tin plate unsuitable for its ultimate use.

Electrolytic tin plate is commercially available in the tin coating weight grades of 0.25, 0.50, and 0.75 pound per base box, now commonly known as No. 25, No. 50, and No. 75. Recent tin restrictions have resulted in production of trial lots of various other coating weights as well as different coating weights on opposite sides. Further development work will be necessary to determine the commercial possibilities of these new classes as means of conserving tin. All coating weight grades may be melted or left unmelted, the latter being known as "matte finish." The matte tin finish is produced with either a smooth temper rolled steel base finish or a satin base finish. This satin base matte finish is a develop-

[d] The unit of measure of tin plate is the "base box". It is equivalent to 112 sheets of 14 x 20 inches, or 31,360 square inches.

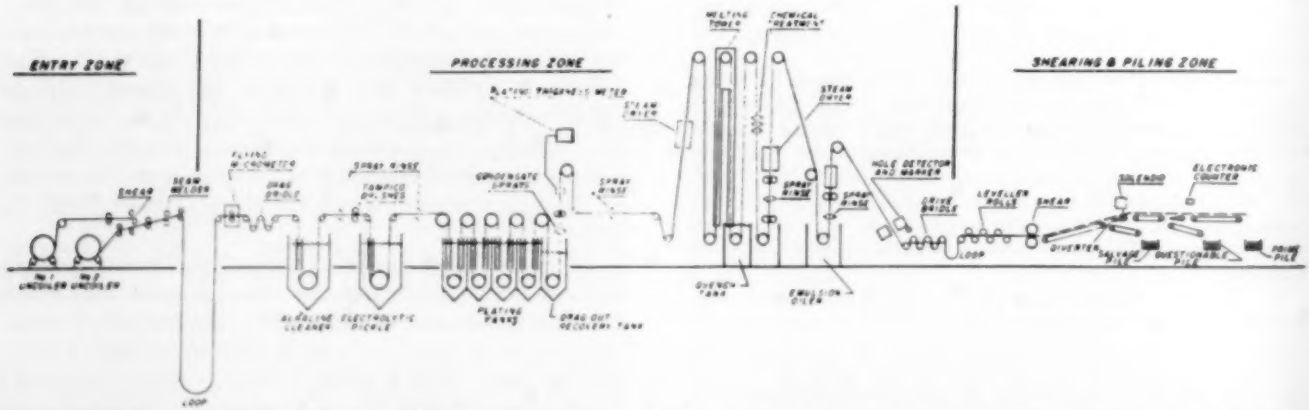

FIGURE 18. U. S. Steel electrolytic tinning line. This detailed sketch shows the number of individual operations which have been incorporated in one continuous operation.

FIGURE 19. U. S. Steel electrolytic tinning line. This view is from entry end of line and from the left shows consecutively uncoiler, welder, looping pit, alkaline cleaner, electrolytic pickler, electroplating tank and melting tower.

ment which is fast gaining in popularity. Most crown caps are now made from this material since its attractive appearance has permitted elimination of certain decorative coatings. In this one outlet alone, considerable savings have accrued to consumers.

In normal times No. 25 electrolytic tin plate was being used for cans for lubricating oils, paints, many other nonfood applications, and for dry food products, such as coffee. Now, No. 25 is specified in N. P. A. Order M-25, dated February 23, 1951, for parts of containers of a number of meat products, some sea foods, certain vegetables, and juices as well as many other foods. In many instances, particularly wet products, this light coating weight requires other protection in the form of decoration or lacquers. The beer can is a good example, with decorating on the outside and lacquers inside. As with all electrolytic plate, the surface is excellent for such operations. Due to its satisfactory performance for many applications and the considerable savings over standard coke hot-dipped plate which was used for the same purposes prior to the electrolytic development, this No. 25 grade constituted more than 50% of all electrolytic plate in 1950.

Prior to the issuance of the N. P. A. Order M-25, No. 50 electrolytic tin plate was used in large quantities for cans of processed food products, such as peas, corn, meats, sardines, and can ends for soup and fruit. Now, as indicated above, many of the vegetables, meats, seafoods, and soups will be packed in containers, part of which will be No. 25. The No. 50 will be retained for specific items in these groups of products and for ends of containers for most fruits where it is felt electrolytic plate can be safely used. For these applications it has been the practice to apply an inside enamel to the plate to provide adequate corrosion resistance.

No. 75 electrolytic tin plate has come into commercial use for sweetened condensed milk cans and for a sizable portion of the evaporated milk pack. From all indications it has been very successful and it appears that this use will expand in the future.

All the electrolytic lines as originally installed prior to 1950 were designed for plating No. 50 coatings at normal operating speeds. This design, therefore, limits the economic production to the lighter coating weights. There is considerable feeling that in order to further substitute electrolytic tin plate for hot-dipped plate, it will be necessary to have a heavier coating grade, perhaps approximating one pound per base box. Serious consideration is being given to the design of lines to electroplate heavier coatings, but frankly, the feasibility of the heavy coating weights has not yet been demonstrated, either from the standpoint of production cost or use.

Corrosion resistance of electrolytic tin plate. Inasmuch as the original electrolytic tin plate was intended for the manufacture of cans and closures for dry products, the principal requirement in respect to corrosion was atmospheric rust prevention. This was fully accomplished at the very beginning with 0.50 pound of tin per base box. As mentioned earlier, the tin conservation program of World War II necessitated the expansion of electrolytic tin plate containers and closures for a wide variety of products, including many wet packs. It soon became apparent that the corrosion resistance of much of the early electrolytic plate was not all that was expected when tested in the "plain condition" with certain corrosive and detinning types of food products. This "plain condition" must be emphasized to prevent misunderstanding, because the inadequacy was not apparent with most of these products when the plate was enameled. To substantiate this latter statement, we need only refer to the many successful applications of enameled light-coated electrolytic plate, including the ends of cans for moderately corrosive fruits and jar caps. Although enameling No. 25 and No. 50 electrolytic plate provided adequate protection under many conditions, extensive corrosion studies were immediately undertaken to determine the full possibilities of this new product.

Much has been known for some time of the part played by the tin and by the steel base upon the internal corrosion of the tin can, but recent investigations have revealed additional important facts which, it now appears, will lead to a higher level of corrosion resistance for any given coating weight. Regardless of these advances, or the unique protection afforded by tin, or the uniformity of tin plated electrolytically, No. 50 will not do the job of coke plate without additional protection by enamels. Therefore, the lighter tin-coated classes must still be enameled to meet most requirements being placed on them today. On the other hand, it is believed that the findings to date, and those which are anticipated, may permit the successful use of somewhat lighter tin coating weights than otherwise would have been possible.

RESEARCH CONTINUES

New processes and devices are still being developed as modern research continues within the industry. Improvements seem to be endless. Although only a few months may separate installation of two pieces of equipment for the same fundamental operation, it is seldom

that one finds exactly the same machine or an identical treatment. This, of course, is the true sign of progress and means better tin plate. Some of the latest development efforts are now taking shape and being placed in operation. Brief mention is made here of some which may be of particular interest.

Electrolytic pickling of hot dipped plate. Electrolytic pickling of sheets in tandem with tin pots has been developed and is now replacing the white pickling operation. This eliminates one of the few remaining heavy manual labor tasks in the production of tin plate. Furthermore, according to Rodgers *(11)*, an improvement in yield of product is also being obtained by eliminating manual handling which often resulted in damaged sheets.

Inspection of hot-dipped plate. The latest method of inspection and assorting of hot-dipped plate, originally developed by the Tennessee Coal, Iron & Railroad Company, consists of a continuous line attached to the tin stack. This mechanical means of handling this operation is being adopted in new plants, while some installations are expected to be made in existing plants. In this method of inspection, the tinned sheets emerging from the tin stack pass over an inspection table or through an inspection wheel and, by means of electrical controls, the inspector can direct the plate into a prime or secondary product piler. Counting is done automatically and packaging is accomplished on a conveyor leading from the prime piler. This new process eliminates several expensive handlings and should result in a better product.

Continuous annealing. During the past several years, attempts have been made to anneal tin plate strip continuously, having in mind replacement of batch annealing shown in Figure 13. Major operating problems and high operating costs have retarded the acceptance of the process. Combining the cleaning operations and development of new heating methods, as well as novel mechanical means for handling long strips of soft steel, have done much to make the operation more practicable. Although many difficult problems still exist, commercial installations are being made, as has been brought out by Martin in another paper in this series *(9)*.

X-ray gages. X-ray gages are now becoming useful in the industry for steel thickness and tin coating thickness measurements.

Trials with the gages are underway on hot-strip mills and cold-reduction mills with the hope of better gage control for these operations. Attempts are also being made to use these instruments for better classification of sheet weights on shear lines than is now possible with contact gages. Problems in adapting the equipment to these mill operations have been encountered, but present advances indicate real possibilities.

Extensive effort has been expended to develop an X-ray method for determining tin coating weights. Some work is also underway with beta-rays. The author is most familiar with the United States Steel's development *(14)* known as the "X-Ray Fluorescence Tin Coating Thickness Gage" (Figure 20), which is now a reality and so the following remarks pertain to it. The method consists essentially of an X-ray beam of proper wave length passing through the tin coating to excite fluorescence in the steel base without interacting appreciably with the tin coating layer. The fluorescent or secondary X-radiation emitted by the steel travels back out through the tin coating and is absorbed to some extent by the tin; the amount of absorption is a quantitative function of the tin coating thickness. This absorption is effectively determined by measuring the intensity of the fluorescent X-radiation which finally emerges from the tin coating by means of a radiation detector,

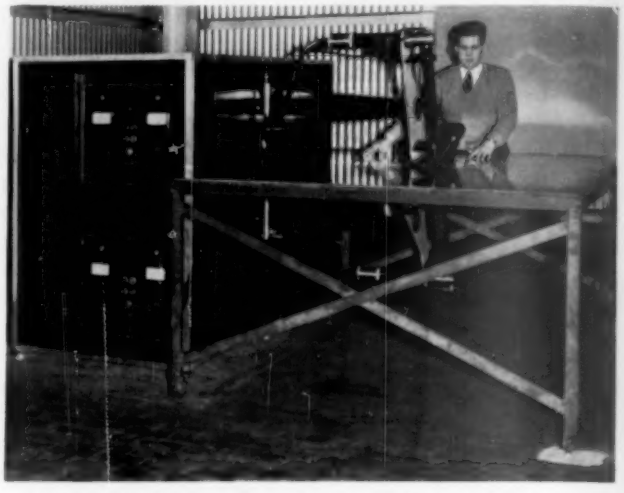

FIGURE 20. X-ray method for tin coating weight determinations. Until recently all of the methods being used for determining tin coating weights were destructive. The X-ray method, which was developed by the Research Department of the U. S. Steel Co., is non-destructive, rapid and accurate.

such as a Geiger counter. Although the equipment for making this test is relatively expensive, its rapidity, convenience, and accuracy are such that it is likely to supersede other methods at mills or laboratories where a large number of such determinations must be made for control or research work. One other important consideration is that the test is nondestructive.

Hole detectors. All are familiar with the occasional hole piercing the base metal of tin mill products and the difficulties which often arise when they escape detection by the tin mill or can making inspection. These holes are caused by small metal particles being rolled into the strip or by a steel surface defect which ruptures at that point during cold reduction or during subsequent fabrication. Several years ago, automatic electric-eye hole detectors were developed by the electrical companies and were soon adopted throughout the tin plate industry. Considerable improvement resulted, but some plate with holes continued to get by. Recent work by the United States Steel Company Research Laboratory has resulted in improving conditions that existed in conventional equipment, such as lack of sensitivity, failure to eliminate holes when they occurred in a closely spaced series, maintenance difficulties, such as frequent lamp burn-out, and nonstandard sensitivity adjustments. The new equipment along with new high speed control circuits, is now in use on several shear lines. Although some holes still may escape detection, significant benefits are expected.

Automatic self-centering rolls. This new invention (Figure 21) is one which would have overcome many problems during the development of continuous tin mill operations, had it come earlier. This, in no way, belittles its value for the future because until now there has never been a completely satisfactory solution to proper tracking and aligning of strip and other materials over and under deflector or conveyor rolls. Many such rolls are necessary, in processing of cold-reduced strip for tin plate through continuous lines for pickling, cleaning, shearing, and electrolytic tinning. The trend toward larger coils and longer strip, increased processing line speeds and longer lines, have aggravated materially these tracking and aligning difficulties.

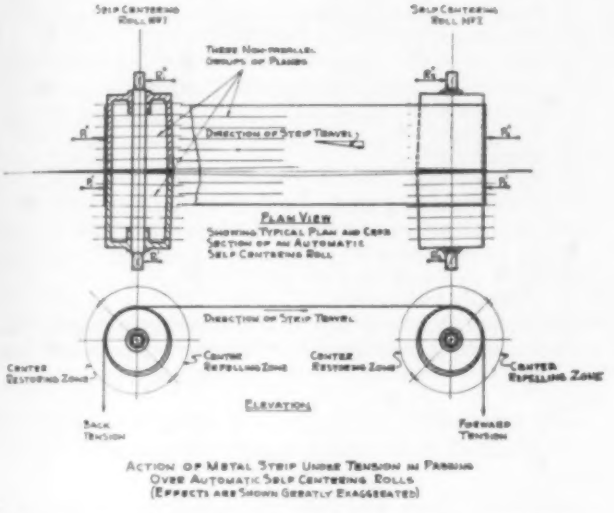
Direction of Strip Travel
Plan View
Showing Typical Plan and Cross Section of an Automatic Self Centering Roll
Direction of Strip Travel
Center Restoring Zone
Center Repelling Zone
Center Restoring Zone
Center Repelling Zone
Elevations
Back Tension
Forward Tension
Action of Metal Strip Under Tension in Passing Over Automatic Self Centering Rolls
(Effects are Shown Greatly Exaggerated)

FIGURE 21. Lorig aligner rolls. One of the most serious problems in design and operation of continuous lines has been to get good tracking of the strip and thus eliminate the weaving tendency. The automatic centering rolls, invented by Mr. E. T. Lorig, of the Engineering Department of the U. S. Steel Co., work on an entirely new principle and appear to have solved the tracking problem. Many new continuous units are being equipped with Lorig Aligner Rolls.

Conventional-type continuous-bodied rolls, with either flat or crowned faces, are not in themselves wholly suitable for tracking and aligning wide, thin metal strip and actually tend toward causing continued divergence of the strip off the pass line of the processing unit as the strip moves forward. Automatic self-centering rolls, developed by Lorig of the United States Steel Company *(8)*, are split transversely at the center. This construction throws the planor action of one-half of the roll out of parallelism with that of the other half under rotation, thereby releasing pent-up natural opposed lateral forces at the roll surface, tending to cause the moving strip to shift laterally toward the center pass line of the processing unit. This centering action is effective under very light strip tensions. Automatic self-centering rolls of the split type, now known as "Lorig aligners," have been in operation in steel processing plants for several months, and very satisfactory results are being reported.

The advantages of this development are not limited to steel strip processing units. Practically every industry where driven conveyor and idler rolls and pulleys are utilized for forwarding strip materials in a definite path, should find economic advantages in the utilization of automatic self-centering rolls or pulleys.

THE FUTURE

Much credit for the accomplishments within the industry and for the promising future is given to the container and canning industries, and also to the manufacturers of tin mill equipment. Their progress is reflected in the progress in the tin plate industry.

In addition to the new equipment and processes just reviewed many other achievements, which will have far reaching effects, are coming into the "production" stage. Still additional promising developments are on the horizon. With these in mind, the industry looks forward to reaching greater heights in respect to both quality and production.

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Significance of Continuous Production Methods in the Manufacture of Tin Plate[a]

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The revolution in manufacturing steel by continuous processing in strip form has had its impact on the manufacture of tinplate. Continuous processing and better control of the operation has made a much superior and relatively cheaper product available. Methods of manufacture of tin plate and the variations introduced in the product in the course of the various steps are discussed.

The tin can is a marvel of man's accomplishment. The modern housewife opens it and tosses it into the garbage pail with a gesture of annoyance. Such is human nature. She is conscious of the slight effort involved and oblivious of the far greater effort she has avoided to secure the food in such healthful, palatable a form whether seasonal or not.

When making his third attempt to discover a Northwest passage from the Atlantic to the Far East in 1824, the arctic explorer Parry was happy to have tin cans for packaging food. To him the tin can was a great invention. It is so common today that few people pause to consider it. Yet the modern tin can is truly more marvelous than was Parry's. It has required years of effort to develop and demands exacting attention during manufacture of the tin plate from which it is made.

Have you ever stopped to consider how complex a section of tin plate is? The various layers in a .50-lb./BB (No. 50) electrolytic tin plate (95-lb. base) are shown in Table 1.

TABLE 1

Relative thickness of layers in section of lacquered .50-lb./BB electrolytic tin plate

	Thickness—inches
Thickness of steel base (95-lb. plate)	.0104
Thickness of tin coating (.50-lb./BB.) (Density = 455-lb./cu. ft.)	.00003
The protecting film on the tin	.0000001 (approx.)
Thickness of oil coating (.20 GR./BB.)	.0000002
Thickness of lacquer (50 mg./sq. in.) (Density = 85-lb./sq. ft.)	.000224 (ave.)

EXPRESSED IN THICKNESS OF STEEL BASE

Tin is 1/347th the thickness of steel base
The protecting film is 1/104,000th the thickness of steel base
Oil is 1/52,000th the thickness of steel base
Lacquer is 1/46th the thickness of steel base

The lacquer film is many times as thick as the tin coating. As you know, the tin coating weight must be closely controlled. But a 10% difference is only 3 millionths of an inch! An oil coating weight of 0.2 g./BB. is about 4 drops of oil, which must be uniformly spread to cover the entire surface of 434 square feet. Give a painter a brush and 4 drops of oil and watch his expression when you tell him to cover 434 square feet of surface. The oil film is not too many molecules thick.

[a] Presented at the Eleventh Annual Meeting of the IFT, New York, N. Y., June 18, 1951.

Now this tin plate must:

1. Be of proper steel base;
2. Have a tin coating of given thickness;
3. Have a uniform tin coating thickness;
4. Have good corrosion resistance;
5. Have good warehouse life;
6. Have the proper oil film;
7. Form a cylindrical can body without paneling;
8. Stamp and draw to the desired shape;
9. Have the proper resistance to buckling under pressure;
10. Provide good adherence for a variety of lacquers;
11. Develop no stain when heated in lacquer baking ovens;
12. Develop no eyeholes in the lacquer applied;
13. Solder well;
14. Lithograph well;
15. Have no holes;
16. Be non-toxic;
17. Be brilliant with good reflectance;
18. Be of proper overall thickness (gauge);
19. Be flat without wavy edges, center buckle or bow;
20. Have no burr from trimming or shearing;
21. Meet size tolerance;
22. Be packaged to resist rusting and damage in transit; and
23. Be made at high speed by continuous methods with huge capital investments to keep the cost down.

The extraordinary thing is that modern tin plate can be made at all with such a variety of stringent requirements.

Inevitably there will be variations in meeting one or more of these many requirements. It is the purpose of this paper to point out the causes for some variations from the ideal and, in so doing, to draw attention to the significance of continuous production methods in making this remarkable product possible.

Brief Summary of Manufacturing Steps. Steel in the form of hot slabs is continuously rolled in hot strip mills to coils each of which weighs many tons. After continuous pickling to remove the surface oxide, these coils are rolled cold at speeds up to 5,000 feet a minute substantially to the finish thickness of tin plate. These mills consist of several stands in tandem between the rolls of which the steel is progressively reduced in thickness.

The cold rolling hardens the steel by its compressing and elongating action and leaves it coated with oil used as a lubricant in rolling. It is necessary to remove the oil by washing. This is done in continuous lines operating at high speeds. The washed steel is softened by annealing in coil form in "box annealing" or, as recently developed, continuously at speeds up to 800 feet a minute. To form the smooth cylindrical bodies of cans the softened steel must be lightly rolled cold in "temper" mills.

The steel base is now ready for the tinning operations by the old hot dipped method, after shearing and side trimming into sheets, or as coils in the more recent electrolytic methods. Pickling in acid to prepare the surface precedes the tinning and, in the case of the elec-

trolytic method of coating with tin, washing may also be done as a preparatory step. Electro-deposited tin is usually melted, "flow brightened" or "fused" to impart certain qualities and to make the surface appearance more reflective and brilliant. Finishing treatments develop particular qualities of the surface which are important in subsequent processing by the can maker.

After careful inspection and "assorting" the finished product is well packaged and shipped to the producers of cans. "Black plate" or steel in the form obtained before tinning is another product while "terne plate" differs by being given a coating of alloyed lead and tin.

With this background, let us now spend a little time in seeking the sources of some of the variations from the ideal tin plate which are of interest to the users of this product.

Variations in Product Introduced During Cold Reduction. When hot rolled and pickled coils are cold reduced by rolling, the finished gauge and shape of the tin plates is substantially determined.

Present day cold reduction mills used in producing tin plate are massive affairs usually having 5 stands in tandem in each of which are two working rolls of 18-20 inches diameter and "back-up" rolls of approximately 49 inches diameter. (Figure 1). These rolls are about 12 feet long bearing to bearing. The function of the "back-up" rolls is to prevent beam-like bending or deflection of the working rolls under the pressures used of over a million pounds.

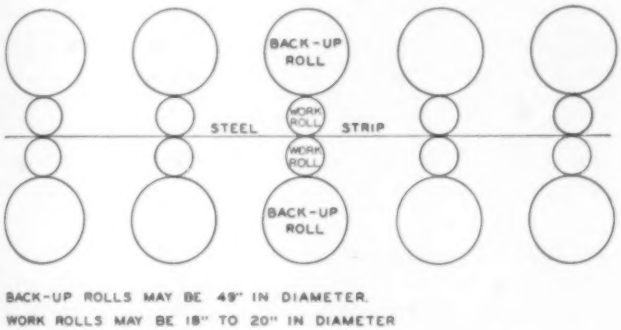

FIG. 1. Schematic drawing of a conventional 5-stand tandem cold-reduction mill.

These mills operate at strip speeds of up to almost 60 miles an hour and roll coils of up to 30,000 pounds in weight and 6 feet high when standing on edge. They are formed by welding together the product of several slabs at the continuous coil pickler. Costing about $8,000,000 each, the mills are supported by an impressive array of electrical and mechanical equipment not visible to the casual visitor. The roller and his crew stand there pushing buttons to direct the movements of this industrial monster created and tamed by man.

Reduction in gauge is accomplished by both pressure from the rolls and tension applied to the strip. Tension elongates the strip which has an accompanying reduction in section like a stretched rubber band.

Principal among the factors affecting gauge and shape are: 1, incoming gauge and shape from the continuous hot strip mills; 2, speed; 3, pressure applied to rolls; 4, distribution of this pressure; 5, tension between stands; 6, shape of rolls; and 7, distribution of lubricant used on steel.

From among these let us select speed for a little closer study. Speed both directly and indirectly affects gauge. Yet in semi-continuous processing, we must bring the mill up to speed and slow it to threading speed for each coil run. The job involved here can be appreciated by realizing the tremendous energy stored in the rolls while at speed. This kinetic energy must be removed and supplied at each deceleration and acceleration of the mill. When the strip is travelling at 4500 feet a minute, this energy is equivalent to more than 230 times the energy released by an automobile weighing 3000 lbs. hitting a concrete wall at 60 miles an hour. This energy is supplied in 6 seconds to accelerate and is taken out in 3 seconds to decelerate. This must be done for each coil, the rolling of which takes less than 7 minutes at speed for a 30,000-lb. coil. Is it any wonder that there exist departures from the ideal gauge and shape?

While this is called cold rolling, approximately 2000 gallons per minute of cold water are used to remove the heat generated while making the reduction in gauge. This heat is developed over only a small part of the faces of the working rolls. The control of the expansion and contraction involved is a very important factor in obtaining proper shape and gauge of the steel strip product of the rolling.

In general, the "heavy ends" of strip out-of-tolerance gauge are produced during the acceleration and deceleration of the mill. These are cut off at some point in subsequent processing. Some variation in gauge and shape may remain in the finished product. It is surprising that the variations are not greater in rolling a hard substance like steel to thicknesses of less than 10 thousandths of an inch.

Variations in Product During Annealing. During cold rolling, the steel is hardened by cold work and must be annealed. This is done either in batches by "box" annealing in the older process or continuously in a method more recently developed.

In the box annealing method several coils laid on their sides are stacked over one another on an annealing base. A cover is placed over the coils to contain the special annealing gases and over several of these coil stacks, grouped on a furnace base, the heating furnace itself is placed. A fan in the base of each coil stack usually recirculates the annealing gases. Heat is commonly generated in radiant tubes by combusting in them gas premixed with air. Radiant energy from these tubes placed in the furnace cover heat the coils through the annealing gas covers.

It is apparent that in this method of annealing, relatively large masses of steel have to be heated through a controlled cycle of temperature versus time. Much of the heat has to penetrate the laps on laps of steel forming the windings of the coil with their intermediate layers of gases. To obtain some uniformity of heating, top temperature is usually reached in about 24 hours while approximately 72 hours are required for the complete cycle.

This is batch treatment, with variations in rates of heating and cooling and with variable accessibility of the

annealing gases from the edge to center of strips wound into coils. The result is some variation of hardness and uneven attack of the annealing gases with ultimate uneven effect on the corrosion resistance of the steel as a base for tin plate.

Continuous annealing of steel strip has been done in relatively slow lines with electrical or radiant tube heating of the strip. Recently, the Inland Steel Company installed a continuous annealing unit, which is running at 600 feet per minute, using radiant gas open cup burners for direct heating of the steel in strip form. Processing in strip form has the advantages of uniform heating across the strip and uniform accessibility of the annealing gases. Rockwell hardness values across the strip show a considerable improvement over box annealing.

The heating and cooling cycle in continuous annealing is very short—a matter of two minutes in Inland's new line compared to hours in box annealing. Actually, most of this short time is taken in cooling since the steel is heated from about 49 to 771° C. (120 to 1400° F.) in 6 seconds. Washing is done continuously in the same line ahead of the annealing step.

The product of continuous annealing has a different combination of physical properties and is at present being made to a single TU, or universal temper, which has substituted so far for a large percentage of box annealed product normally supplied in six temper ranges. The ultimate field for continuously annealed tin plate has not been definitely established. New lines are being built or are being considered by other companies in the steel industry.

Variations in Product Introduced During Tin Coating. Hot-dip tin plate has a relatively non-uniform coating weight. The applied tin is molded, while solidifying, to a hill and valley surface topography by the oil-run-off and rather sharp variations in average thickness of the tin coating occur over the surface of a tin plate. Some tin is carried over from the last set of tinning rolls in a tinning machine and solidified on the trailing or "drip edge" of the plate. The variability of tin coating weight over the surface of hot-dip tin plate is expressed in the following quotation from the American Iron and Steel Institutes' Steel Products Manual, Section 14, "Tin Mill Products":

> "On hot dipped tin plate, the coating is mechanically distributed over the sheet surface by tinning rolls. Due to the nature of the hot tinning operation and the elevated temperature of the tin metal it is not possible to control, within close limits, the tin coating weight on individual sheets and from sheet to sheet."

The Institute's suggestions for sampling follows:

> "When coating weight check tests are conducted on a shipment of any specific item of hot dipped tin plate, based on experience the following procedure is recommended:
>
> "One plate is taken at random from each 50 packages, with a minimum of three sample plates, each taken from different multi-package units from any one item of a specific shipment. Each sample is spot-tested at three positions taken on a diagonal across the plate. Spot samples are customarily discs or squares, each of 4 sq. in. area. In order to secure representative samples they are taken so that the outer edge of the sample is at least one inch from any edge of the plate. The average value of all spot tests on all plates tested represents the average coating weight test value."
>
> "The coating weight in localized areas on occasional sheets, as determined by spot samples selected in the manner described under the recommended sampling procedure, deviates as much as 0.25 lb. per base box under the values shown in Table 2. Exceptional instances of even lower coated areas sometimes occur."

TABLE 2

Tin coating weight test values

Class designation	Minimum average coating weight test value, lbs. per base box
Common cokes (1.25 lb. pot yield)	0.85
Standard cokes (1.50 lb. pot yield)	1.05
Best cokes	1.19
Kanners special cokes	1.40
1A charcoal	1.80
2A charcoal	2.30
3A charcoal	2.80
4A charcoal	3.50
5A charcoal	4.20
Premier charcoal	4.90

The more recent electrolytic tin plate carries a more uniform coating weight. (See Figure 2 for a typical example.) The hill and valley effect found on hot-dip tin plate does not exist. In general there is a tendency to a heavier coating near the edges.

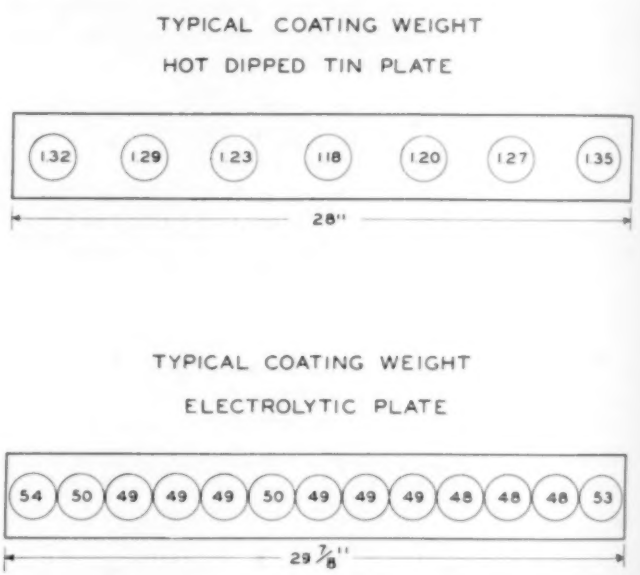

FIG. 2. Typical coating weights on hot dipped and electrolytic tin plate.

There are several types of electrotinning lines. In one, the so-called alkaline type, the anodes used for plating may weigh three tons or better. An illustration of one type of such anode is shown in Figure 3. One of these anodes is suspended between the passes of vertically moving steel strip in such a way that both sides of the strip are plated with tin simultaneously. Since these anodes must serve for all widths of strip processed, they are designed to give a little heavier coating weight at the edges for most widths. If the strip wanders a little from the central pass line, one edge of the finished plate may possess a slightly higher coating weight than the other.

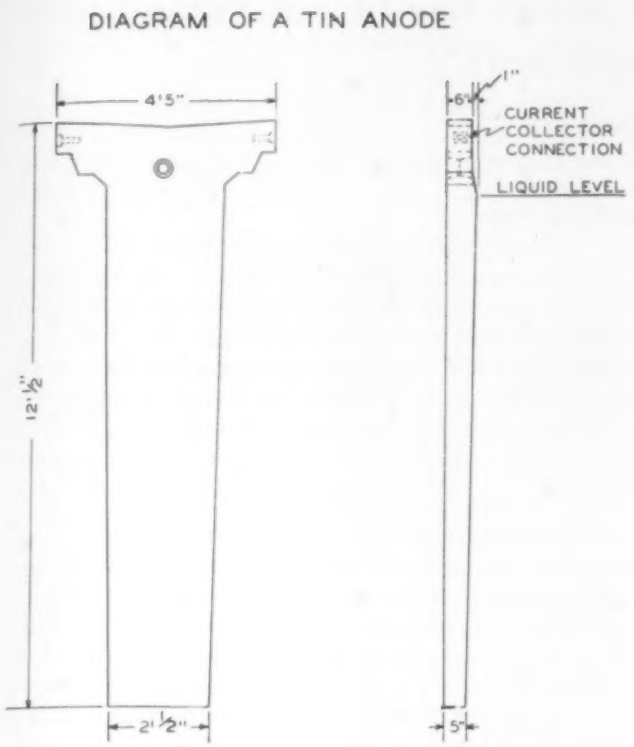

FIG. 3. Diagram of a tin anode used in the alkaline type of electrotinning line.

The alkaline tin plating baths in use have excellent throwing power, or ability to plate uniformly over a considerable area. In some other lines smaller anodes are used and must be very carefully disposed with regard to the steel strip to secure a uniform coating weight.

It must be remembered that these lines are plating tin on strip running continuously at from 500 to 2000 feet a minute. This is by far the most spectacular application of electroplating in all industry.

Variations in Product Introduced by Finishing Treatments. Finishing treatments are treatments given the electrolytic tin plate strip after coating, melting, and solidification of the tin applied.

They are designed to improve warehouse life and assist in providing a surface to which a variety of lacquers will adhere and which will not discolor in lacquer baking ovens. These three properties are not always attained together. Sometimes to obtain extra good performance in warehouse life, lacquer adherence is sacrificed to some extent. The reverse is also true.

A variety of treatments exist. Some of these are purely chemical dip treatments, some are electrolytic and some are a combination of electrolytic and chemical dip treatments. This is a delicate field because we are dealing with the character of tin oxide or other tin salt on the surface of the tin whose thickness is measured in terms of millionths of an inch.

Continuous Strip Processing and Better Control Have Yielded a Better Product. Machines are better than men in doing the same thing exactly the same way over and over again. Batch processes have variations from batch to batch. The more continuous the operation, the greater the uniformity of product. Handling steel as long ribbons wound on spools provided greater continuity of operation than handling and processing as sheets. Joining the ends of these ribbons to form a continuous "strip" of steel with provision for enough storage capacity of this strip to permit the operation to proceed continuously at speed while joining the ends, has permitted continuous instead of semi-continuous processing with intermediate handling of the steel between operations in the form of spools or coils.

Today, hot and cold rolling, pickling, and washing are semi-continuous; although larger and larger (now 30,000-lb.) coils are being processed by welding the strip product of several steel slabs together to form larger coils. This provides longer running time between stops in semi-continuous operation. Annealing is batch (old) and continuous (new). Hot-dip tinning is by individual sheets; electrolytic tinning is continuous.

What, you ask, is the ultimate outcome? Will we perform all operations that are necessary successively on one long continuous strip? It is unlikely. We must realize that reliability or percent of total time actually running is a very important factor. Each step incorporated in the continuous processing line is a potential source of stops. In the modern electrotinning line we have combined operations which are separately performed in making hot-dip tin plate. Some lines have combined trimming of the edges, pickling, plating and "fusing" or "flow brightening," surface finishing treatments, oiling and shearing. All are done successively without stopping the strip. Continuous annealing has incorporated with it preliminary washing of the strip.

Methods of control have progressed rapidly with this trend. In fact electric drives and the development of synchronization of parts through electric controls were necessary preludes to the current revolution in steel processing. When speeds passed the ability of mechanical gauges, x-ray gauges were developed.

With continuous processing and better controls of many kinds, the way has been cleared for a much better product of greater uniformity to assist subsequent processing: a better product at lower cost!

So the fiery, massive steel mill has turned into a workshop of delicate artistry holding to almost unbelievable limits in making electrolytic tin plate while revolving huge rolls at ever increasing speeds. The giant trained to thread a diminutive needle!

CONCLUSION

The revolution in manufacturing steel by continuous processing in strip form had its impact on the manufacture of tin plate. Continuous processing and better control of the operation have made a much superior and relatively cheaper product.

Manufacture in the United States of these complex tin mill products of so many stringent requirements is an important business which has demanded a tremendous investment by the steel industry. Producing now at the rate of 5,300,000 tons a year of tin mill products, the United States used for this purpose more steel than is produced for all uses by any other country except Russia, the United Kingdom, France, and Germany.

Corrosion Factors Related to the Use of Tin Plate for Food Containers[a]

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The mechanism of internal corrosion in tin plate containers is described and the factors which affect corrosion, such as the product packed and the effect of the tin plate and steel base on shelf life, are discussed. The problems of tin plate testing are indicated.

There are a number of considerations important to the manufacturer and user of tin plate. Each of these deserves to be discussed in considerable detail because it is important to the proper understanding and successful use of tin plate containers. However, a complete catalogue of these factors and the manner in which they affect relationships between tin plate manufacturer, can maker, and canner cannot very well be made in a reasonable length of time and one phase only, the internal corrosion of tin plate containers, has been selected for the subject of this paper. Any one of several reasons might be cited for this selection. Adequate resistance to internal corrosion is certainly one of the more important performance requirements of tin plate containers because in contrast to other tin plate properties, failure is not immediately obvious but is delayed until a time when much is at stake. It is the phase about which there are many misconceptions. It is also one of the places where outstanding progress has been made and finally, since it is the chief factor in determining how little tin can be used, it is a timely subject.

Corrosion in tin plate containers may carry different meanings to different individuals. Some have been concerned only with the appearance of the container or some other particular phenomenon, but the usual meaning, and the one adopted here, refers to the total of all processes involved in the interaction between product and container which ultimately results in the formation of hydrogen swells or perforation, either of which makes the container unsalable. The measure of performance is the length of time required to reach this state, and is usually referred to as the "corrosion shelf life." In contrast to the situation existing twenty years ago, few foods present a critical problem but since corrosion occurs to some degree in all, the commercial aspect is maintaining the shelf life at or beyond a point permitting orderly marketing and consumption of the pack.

FACTORS AFFECTING CORROSION SHELF LIFE OF TIN PLATE CONTAINERS

It may appear strange at the outset of a discussion on tin plate to emphasize the fact that it is not possible to consider the internal corrosion of food containers as a matter related solely to the container material. On the contrary, it is a problem affected by two sets of factors, one concerning tin plate and container and the second, the product and the circumstances surrounding its packaging and subsequent handling. The commercial importance of the latter may be judged by the fact that a classification of food products was a necessary preliminary to the development of successful tin plate specifications *(1)*. It may also help furnish a better perspective to realize that some twenty years ago there were a number of food products for which an adequately corrosion resistant container was not available, no matter what was done in packaging the food. Today, with few exceptions, containers having properties permitting orderly marketing are available for each product, but it is possible to reduce their performance to that of the earlier period by the factors associated with the food. It should be more widely appreciated that in contrast to popular opinion on the subject, tin plate alone is incapable of solving all corrosion problems.

The number of processed food products packed in tin plate containers exhibits a wide range of corrosive characteristics. The causes of these variations are not fully known, but considering the nature of the ultimate result and the fact that most foods are on the acid side of pH 7, it seems apparent that acidity should be an imporant variable. While it is true that many of the most corrosive foods are also the most acid, it does not follow that corrosion is proportional to acidity for some of the less acid fruits have been among the most difficult to handle. Because of this observation it has been suggested that there might well be a maximum corrosion rate near pH 4, and consequently increasing acidity could on occasion inhibit corrosion. While addition of food acids to some products has accomplished this, in others the opposite result has been obtained, so the concept of an optimum pH does not appear to be a general principle. The specific acid present has in some cases been known to have its own characteristic effect, but neither a knowledge of the amount and type of acid nor the limited information available on other corrosion accelerators or inhibitors as yet permits prediction of corrosivity and experience is currently the only demonstrated sound basis for judgment.

While the usual interest is in the intensity of corrosion, it is important for an understanding of the process to realize that all foods do not produce the same type of attack on tin plate. Experience has shown that some foods tend to be more reactive with tin than others and this characteristic does not necessarily have any particular relationship to the length of shelf life. Other foods have a more pronounced tendency to center corrosion on the steel base while still others show no marked trend in either direction, and some show both. Regardless of which tendency is involved, nearly all

[a] Presented at the Eleventh Annual Meeting of the IFT, New York, N. Y., June 18, 1951.

normally have one factor in common: in their presence tin is able to furnish electrochemical protection to the steel base and thus inhibit its corrosion. This characteristic is at the heart of any study of internal corrosion in tin plate containers and helps to explain the leading position that tin plate has held for many years as a food container material.

CORROSION MECHANISM IN TIN PLATE CONTAINERS

In the sense that there is no agreement on why this is so, it may be said that the phenomenon is imperfectly understood and on occasion there has been considerable comment on the fact that inside the food containers tin and iron do not usually exhibit the potential relationships indicated by the standard electrochemical series of the elements. Since the latter is based on metal concentrations in the solution which do not prevail inside a container, the reversal of the usual relationship should not be particularly surprising. The fact that this could occur in acid solutions was reported by at least two scientists, including Faraday, more than one hundred years ago and it was necessary to rediscover it in the late 1920s before sound progress on the corrosion problem could be made. Regardless of these considerations, the important point is simply the existence of this relationship within a container for if this were not so, tin plate containers for fruits and similar foods would fail in a very short time. It may be said that from the corrosion viewpoint there is more to the particular desirability of tin plate for food containers than the anodic relationship of tin to iron, for several other metals and alloys would be expected to possess this characteristic. Tin itself, in the absence of air, is usefully resistant to direct attack by food products and it is the combination of these two properties which makes tin plate better suited to a larger range of products than any currently available coated steel product.

The usual concept of corrosion within a container is a process wherein tin dissolves and hydrogen deposits to polarize the exposed steel areas, tending to protect them from attack. The production of gaseous hydrogen from that deposited is thought to be slow and this reaction thereby controls the process so the protective influence of tin is extended over a period of time. While this leads to the thought that the vacuum in a container should be dissipated at a nearly linear rate, this does not actually occur, or in other words no significant amount of gaseous hydrogen from solution of the tin accumulates within the container. Which one of the several possibilities accounts for the apparent disappearance is unknown but assuming satisfactory steels and normal products, the typical corrosion history in a plain fruit can consists of a protracted period of slow and usually insignificant vacuum loss after which corrosion proceeds at an accelerating rate until a hydrogen swell is produced. The point of acceleration corresponds to the time at which there has been sufficient dissolution of the tin coating so that it begins to lose its effectiveness and at the time of failure it has nearly completely disappeared. The ideal in container corrosion may then be described as a process where tin is protective for a maximum time and no solution of the steel base takes place until the available tin is exhausted.

This tendency is naturally most marked in the type of foods best illustrating the concepts outlined above, such as most fruits packed in plain cans. It will be recognized that many factors can modify the actual course of events. It is clear that if a food possesses a special property to react with tin, the amount of the latter available for electrochemical protection of the steel will be reduced. Enameled containers would tend to counteract such conditions, but simultaneously change the relative amounts of tin and iron involved. The presence of trace amounts of such elements as sulphur or certain of its compounds may prevent tin from exerting its protective effect and there are many other factors which tend to prevent the ideal situation described above. However, from the tin plate viewpoint, the important consideration is that the protection afforded to the steel is never perfect. It is usually considered that this results from the heterogenous nature of the exposed steel which tends to produce local cell action at these points. This tendency is reduced by the protective effect of the tin, but it is not entirely suppressed and may be reflected in an increased solution of iron, possibly progressing to noticeable pitting. It may also induce a more rapid dissolution of the tin coating which permits general attack of the steel base at an earlier than normal time. Whichever occurs, it will be recognized that the cause is the same, namely, the effectiveness with which the steel can be protected under the particular conditions encountered. It will also be seen that a relatively high iron content is the characteristic that all corrosion failures have in common and that the tin may be either high or low, depending on conditions.

EFFECT OF TIN COATING ON SHELF LIFE

By now it will have become apparent that so far as tin plate alone is concerned, two sets of factors influence the corrosion shelf life of containers. Since the effective source of hydrogen in a can is the iron, one set of these pertains to the steel base. Similarly, if tin is the source of protection for the steel base, it is possible for anything affecting the coating to influence the results. Of the two, the tin is of more immediate interest in view of the restrictions on its use during the past ten years, and the most obvious variable is the amount present.

It is difficult to state any general principle on the effect of tin coating weight in a few words because it depends on how it is used, for what product, whether abnormal corrosive characteristics are present, and in many cases, the nature of the steel involved. Prior to restrictions on tin, most interest in the effect of tin coating was confined to what have been termed as "moderately" and "strongly" corrosive products (which include all fruit products and other foods of an acid character) because these provided the major commercial problem. For these products and many in the mildly corrosive class such as tomatoes for which either fully plain or fully enameled cans were used depending upon the product requirement, the prevailing opinion of workers in the field is that the effect of tin coating weight on shelf life is for practical purposes directly

proportional to the amount present. This statement presumes normal corrosive characteristics in the food as well as the same, and satisfactory, steels for the purpose. There is probably no better illustration of the necessity for the latter as well as the relative importance of tin and steel for some uses than that contained in a report of experiments with coke and charcoal coatings on steel of varied ancestry *(2)*. In three successive years, using different lots of tin plate, it was found that charcoal plate either furnished a better shelf life than coke plate in about the expected amount, was about equal, or was considerably poorer. There is another report in which one lot of steel with a 0.8 lb. coating [b] gave as good results as another with 2.9 lb. coating *(4)*. In the face of this type of information it is difficult to understand a widely held view to the effect that tin coating is the only tin plate property important to its corrosion resistance and that amounts above a certain level invariably assure success while those below it always result in failure.

With the necessity to use lightly coated electrolytic plate which was considered to have the best prospects for the least corrosive products came the realization that the direct proportionality between tin coating and shelf life did not apply in enameled cans for many foods in this category. It can be demonstrated that a change in tin coating weight makes only minor differences in corrosion shelf life for this type of product, performance differences between 1.25 and 50 hot-dipped plate enameled pea and corn cans ranging from nothing to 20%, for example. This principle holds for many meat, fish, and vegetable products.

Another condition under which tin coating makes no significant difference in the corrosion shelf life occurs in the case of the so-called "combination" can; that is, a container with a plain hot-dipped body and enameled electrolytic end. The success of this type of container where used to replace the plain container made entirely from hot-dipped plate appears to depend upon the fact that the body is capable of furnishing protection to the end. Under these conditions the tin coating weight on the ends may be varied widely with no effect on shelf life. In fact, such containers with enameled electrolytic ends often out-perform the complete hot-dipped can.

A final consideration with regard to the relative value of tin coating lies in the difference between plain and enameled containers, where both can be used for a particular food product. Prior to World War II, there were a number of foods and meat and fish products in particular where it was conventional to employ plain hot dipped plate. Due to the type of corrosive characteristics of these foods it was found that enameled electrolytic plate could be used with at least equally good results and there are a number of products such as dog food where it can be demonstrated that enameled No. 25 plate cans have a longer shelf life than the plain hot-dipped plate used at one time.

The ability to use enameled electrolytic plate in the manner outlined above must not lead to the conclusion that enameled cans out-perform plain cans for all products. While such applications have probably been the largest single tin conservation measure, a review of the literature of an earlier period will show that the usual comment on the relative behavior of the two types of containers referred to a greater corrosion hazard in enameled cans. These two statements are not contradictory, as they may first appear, because they concern different types of products, the earlier references being principally to fruits. In other words, whether a plain or an enameled can has a longer shelf life depends upon the corrosive characteristics of the product packed and it can be shown that the nature of the steel and the tin coating weights involved also have a bearing on the matter. It may be said that the earlier comments regarding the risks in enameled fruit cans do not apply with equal force today because the steels used are so much better adapted to the purpose.

Porosity is the other factor concerning tin coatings which has attracted great interest. Much has been made of the fact that tin coatings are not perfectly continuous and that this property has been considered by some to be the factor controlling internal corrosion. Porosity of tin coatings has been measured frequently and it is known to be related to tin coating weight, but although it is greater for lighter coating weights, even the heaviest coatings commercially available are not pore-free. The actual amount of iron exposed has been reported in the order of 0.67 sq. mm./sq. meter in 1.5 lb. coatings *(3)* and is a far smaller figure than popularly supposed. It may well seem strange that belief in the importance of porosity should have gained such a firm foothold, for in spite of the many comments in the literature to this effect, no evidence has been cited to substantiate it. Several observers have concluded that its importance was overstressed and data are available *(5)* indicating that it is not a major factor in internal corrosion of tin plate containers. This should be expected, for, as previously pointed out, the principal controlling factor in corrosion of the tin-iron couple type in a can is thought to be the ease with which hydrogen can be discharged at the exposed steel areas. Thus the quality of these sites should be much more important than their quantity. Probably the best practical assessment of the role of porosity lies in the fact that control of this factor was not even attempted in effecting the shelf life improvements obtained in tin plate during the last twenty years.

It is desirable to point out here that, in contrast to the interior, it is only under rarely found conditions that steel on the outside of a can is afforded electrochemical protection by the tin. The results of exposure to external corrosive conditions usually appear as rust and as a general principle it may be said that the time required to produce rusting of plain tin plate is closely proportional to the tin coating weight, other factors re-

[b] The base box (112 sheets of 14 x 20 inches or 31,360 square inches) is the unit of area in the tin plate industry and tin coating determinations are customarily reported in pounds per base box (BB). Thus No. 100, No. 75, No. 50, and No. 25 are terms used to denote electrolytic tin plate which carries 1.00, 0.75, 0.50, or 0.25 lbs./BB of tin, respectively. Hot-dipped coatings are known as "cokes" or "charcoals," the former term referring to coatings under 2#/BB. The two lightest cokes are referred to as "1.25" and "1.50" plate, but here the terms refer to the amount of tin required to make the plate rather than that actually present on the sheet used, which is necessarily somewhat less.

maining the same. However, it is seldom that the relative rust resistance is of more than academic interest for the important matter is whether any given coating weight is adequate under the conditions of its use, a point which cannot be determined in the laboratory.

Practical experience suggests that tin plate is not a particularly rust-resistant material and that, as pointed out in 1917 *(4)*, the conditions under which it is exposed are far more important in determining whether it will rust than the amount of tin coating. Such commercial experience as the several years of successful use of No. 25 outside plain cans for dog food, shortening, and coffee suggests that any tin coating weight of this amount or more can be used plain if conditions are normal, and that when rusting is encountered its elimination lies in correcting the conditions responsible or in the use of enamel coatings. No instance is known of an increase in tin coating eliminating the type of rusting troubles of concern to the packer, and it is interesting to note that when investigating rusting of "combination" cans it is the usual experience to find rusted hot dipped parts among the samples.

In view of the importance of steel to the internal corrosion process, it should be said that the types commercially furnished bear no particular relationships to the incidence of external rusting.

EFFECT OF STEEL BASE ON SHELF LIFE

Being the source of hydrogen in corrosion losses, the steel base of tin plate has received considerable attention. There are a number of reports available on this factor, some of which at first appear contradictory. Partly as a result of this, and partly because of the failure to appreciate that corrosion is not a matter to be considered by itself but rather as related to the particular food product, there is a considerable misunderstanding of the effect that steel may have.

The basic requirement appears to be for a steel which can be given efficient electrochemical protection by tin under the conditions of its use. This is so easily obtained with those products which experience has shown to be mildly corrosive to tin plate that great variations are required in the steel to make detectable differences in shelf life and it has been pointed out that most of the steels available twenty years ago were satisfactory for this class of foods *(1)*. With the moderately and strongly corrosive products, in which corrosion losses were fairly frequent twenty years ago, steel is the most important factor about tin plate and it appears that as a rule the most corrosive products are those in which it is most difficult to furnish effective protection to the base metal. It seems clear that under these conditions there can be no good agreement between different investigators or the effects of variation in the steel base unless the food products involved are the same and this does much to explain the varying reports on the subject. It will also be apparent that conditions leading to large shelf life variations in some strongly corrosive products may be of no consequence for less corrosive foods. In other words, there is nothing to be gained by unnecesary restrictions on types of steel for containers because this may not only fail to secure any shelf life improvement, but it may actually result in an impairment of other tin plate properties which may be necessary for the intended use.

The most obvious characteristic of steel which could contribute to shelf life variations is its composition. Much has been published on this subject and the history of the changes made during the past twenty years, as well as the threefold or more shelf life improvement effected in some cases, is a matter of record. It may be noted that this was a period of experimentation not only with tin plate, but with representative types of the various foods involved as well and of successively finding and eliminating individual detrimental elements until a satisfactorily high level of performance was reached. To be certain that other variations which might occur do not cloud the issue, it is most desirable that such work begin in the steel plant with samples of the same steel differing only in the elements desired and processed together not only to the final tin plate but through all stages of can manufacture, packing, and storage as well. Such work is necessarily time consuming, but in this manner and with the assistance of the steel industry, the effects of nearly every element known to be present in significant amounts in tin plate steel has been evaluated.

In the article tracing the development of better steel *(1)*, silicon, phosphorus, copper, nickel, chromium, molybdenum, and other unspecified elements are mentioned as having been controlled to provide maximum performance for the most critical uses. Data on the effect of many of these and other elements, such as carbon, manganese, and sulphur have been published and, as previously mentioned, are not in complete agreement. The effects of steel composition have already been referred to in a previous paper in this group, but at the risk of some duplication, this topic deserves further mention. Current opinion in this country is that there is no need for more than the broadest of controls over carbon, manganese, and sulphur and that in general the ranges satisfactory for good mechanical properties and representative of standard practice for many years are also satisfactory from the standpoint of shelf life. When used in sufficient amounts, all the other elements named have been known to reduce corrosion resistance to low values with some food products. The most detrimental of these elements is silicon, which was involved in a large corrosion loss shortly after 1930 *(1)*, and as a result no tin plate steel specification for food containers has for many years allowed more than residual amounts of this element, usually considered as 0.01% or less. The effect of phosphorus is most noticeable in the strongly corrosive class of foods, particularly in fully enameled cans, such as those for red cherries, where a change from 0.015% or less to some 0.06-0.08% may reduce shelf life to one-third of its expected value. Since addition of phosphorus is one of the best ways to strengthen tin plate steel to the point required to withstand the high temperature processes required for the mildly corrosive products such as peas and corn, it is fortunate that this element has no effect on the shelf

life of containers for such uses. The other elements named can have detrimental effects of the same order as phosphorus, but these are confined to the strongly corrosive products and no instance is known where any of them had an adverse effect on the shelf life of cans for moderately or mildly corrosive foods. Furthermore, these elements do not have a uniformly undesirable effect, but many affect only a few members of the strongly corrosive class of foods and one, copper, having a dual role. Where detrimental, as it is with red cherries, variation in the amount of this element can have as large an effect as phosphorus, but comparable variations can improve the shelf life of cans for such other products as loganberries. On occasion a 50 to 100% improvement may result.

For most other uses to which steel is put, there is more to manufacturing a satisfactory finished product than its composition and the same may be said with regard to tin plate. While a number of suggestions has been made, nothing has been published which could very well serve as a standard for the various points in the tin plate manufacturing process which conceivably could have an influence on the performance of the final product. In view of this, it need only be said that, like steel composition, virtually every phase of the process has been and continues to be investigated with a view of minimizing factors responsible for variation in performance.

Excluding tin plate for special purposes, the net results of these investigations, combined with the collaborative efforts of the steel industry are today reflected in three kinds, or "types," of steel known as L, MR, and MC. The precise composition of these materials cannot very well be given because they are not necessarily made to the same specifications for each user, reflecting the fact that there can be differences of opinion in the translation of experimental data to commercial practice. The important point is that whatever their compositions, these types represent whatever the particular concern has found by experiment to produce satisfactory results. It is generally known that type L plate is that ordinarily used for the strongly corrosive products so this steel carries the most rigorous restrictions on composition. The intent of type MR is to furnish the benefits of low phosphorus steel for uses where small amounts of nonferrous metals are of no consequence and MC, containing added phosphorus for strength, is for applications where neither this nor other residual elements matter.

It may be noted that neither of the low phosphorus steel types could have been made on a practicable scale by the hot-rolling process of tin plate manufacture. In other words, the practical realization of the benefits of research on tin plate corrosion are available only because the steel industry, at a great cost, revolutionized the manufacturing process. It will also be apparent that without the ability to produce continuous strips of steel, electroplating would not be a practicable process and consequently there would be only a minor degree of tin conservation possible today, available through the adjustment of hot tinning pots.

ELECTROLYTIC TIN PLATE

Since the largest part of the tin plate used today is made by the electrolytic process, this material deserves special mention. The fact that for certain uses the light No. 25 and No. 50 coatings can be employed in the enameled form to replace hot-dipped plate with satisfactory results has already been mentioned and naturally this is known to every tin plate user. Less widely known is the reason for the much limited use of heavier coatings which could be used plain. Reluctance to make practical application of plain electrolytic plate with coating heavier than No. 50 dates back nearly ten years when in the course of work on tin conservation during World War II it was found that heavily coated electrolytic tin plate frequently gave as long a shelf life as hot dipped plate, but just as frequently furnished only a small fraction of it. It was quite apparent that material with such erratic corrosion behavior could be employed in plain cans for processed food products only under certain special conditions where very mildly corrosive products were involved.

Since that time research, both on the part of the tin plate producers and can manufacturers, has been carried on continuously in an effort to find and correct the cause of the variation in corrosion resistant properties. A good part, at least, of the reason for the erratic corrosion behavior of plain electrolytic cans is known to be associated with the surface of the steel. One prominent factor in the problem is the presence of what appears to be a surface layer of metal affected by the annealing process. Although no obvious signs of such a condition appear in the bright steel base, this can be demonstrated and is measured by immersion in hot, dilute hydrochloric acid, absence of the condition being denoted by a linear rate of attack on the steel. Presence of this factor results in an initial inhibition or "lag" in rate of acid attack, the degree varying with the thickness of the affected layer which as judged by this method may on occasion easily reach 30 or 40 millionths of an inch and assuming all other factors remain the same, increasing "lags" correlate with decreasing shelf life. Oxidizing influences during annealing appear to be responsible for this effect. Several tin plate manufacturers have spent large sums for annealing atmospheres which do much to correct the condition in box-annealed steel.

Partly because the shelf life variation in plain electrolytic cans is greater than in hot dipped plate cans in spite of the fact that the condition described above has always existed in the latter, it is believed that additional steel surface problems of a more subtle nature exist. These are thought to reflect the fact that what is accomplished on the electrotinning line prior to tin deposition does not always furnish the same result as the pickling and fluxing to which the steel for hot dipped tin plate is subjected.

It may be said that the average corrosion-resisting quality of plain electrolytic plate has improved markedly since its introduction, although much the same spread in extreme results still exists because measures to counteract the above conditions have not been uniformly adopted throughout the industry. An early practical

solution to these problems is to be hoped for because it should then be possible for many uses to obtain with electrolytic tin plate a shelf life at least equal of that furnished by the somewhat heavier hot-dipped plate manufactured in past years.

It should be emphasized that the effects described above apply only to plain electrolytic tin plate cans, and that they have nothing to do with the use of enameled electrolytic plate in its current applications where consistently satisfactory results are being obtained.

TIN PLATE TESTING

There is a widely held opinion among many individuals producing or consuming tin plate that lack of quick and accurate means of determining the corrosion resistant properties of tin plate for any use represents a conspicuous failure on the part of those working on this problem. For this reason it is desirable to consider the subject briefly here. The reason for the failure to reach this ideal is not lack of appreciation of such a need, but rather the previously mentioned point that the corrosion resistant characteristics of tin plate cannot be considered as absolute properties in themselves, but only in relation to the intended use. When the wide variety of corrosive characteristics in the large number of different foods packed in tin plate containers is considered together with the types of containers manufactured, it can be seen that the possibilities of obtaining a single test to evaluate tin plate for all purposes is no better than for any other corrosion resistant material.

A number of such tests have been devised for tin plate. The only one of these attempting a simultaneous measure of steel and tin coating and which has attained any widespread use is the "hydrogen evolution" test, where an attempt is made to simulate conditions existing in fruit cans *(6)*. It has been made clear that there are limits to the significance which may be placed on test results, and that there are limitations to the test which was devised to screen out plate capable of causing early corrosion losses in fruit cans. In spite of this the impression has arisen that plate superior in this test is also superior in vegetable, meat, and fish cans, as well as for other uses. It should be made clear that the hydrogen evolution test is considered of value only where correlating data from experimental packs indicate a significant relationship. Although with certain qualifications such a relationship exists for fruit products, there is no reason to believe that it extends to all foods in general, or to other specific corrosion phenomena, such as rusting. In fact, available information indicates that it does not.

Since there is not likely to be any all-purpose test for tin plate, it is the opinion of many workers that effective testing will ultimately be a matter of measuring the individual factors or special properties shown to be important to the particular use. It will be recognized that this was the basic technique used in obtaining better tin plate steel and that measures such as the hydrogen evolution test have served more to confirm the expected result than to indicate the direction for improvement. In the long run it must be determined by experimentation what factors, such as steel compositions, etc., are important to any particular application. In other words, factors important to one tin plate use are not necessarily important to another and for this reason each user must devise his own tests. Judging by published reports from earlier years, it is surprising how many have lost sight of the fact that to be of any value, tests must be demonstrated to correlate with the end results desired.

SUMMARY

In summary it may be said there is no simple set of rules which permits evaluation of corrosion factors related to the use of tin plate for processed food containers. This situation arises from the fact that both the product itself and the tin plate, as well as the manner in which the tin plate is used, contribute to the end result. Corrosive characteristics of food products vary widely and for these reasons actual trials and experience from similar products are currently the only known methods of determining the relationships between shelf life, product, tin plate, and container. Although variation in the product itself may provide a degree of corrosiveness which cannot be compensated for by tin plate, the practical advances of the past twenty years have been attained by the manufacture of better tin plate.

The technical basis for success of tin plate as a container material lies in the ability of the tin coating to afford electrochemical protection to the steel base while itself remaining usefully resistant to the corrosive action of food products. In spite of this, corrosion failures are the result of interaction between the product and steel base and therefore both the amount of tin and nature of the steel influence the corrosion shelf life. The effect of variation in tin coating weight depends on the type of container in which they are used as well as on the steel and product. The effect of steel composition or variation in other characteristics depends on the use to which the tin plate is put, being very important in some instances and of no practical importance in others.

There are a number of misconceptions regarding the properties and role of tin plate as related to the shelf life of containers. The value of tin plate for this purpose cannot be measured by tin coating alone nor is there any given coating weight which is sufficient by itself to assure success for all purposes against all other factors influencing performance. Tin coating porosity is no criterion of performance. There is no single steel composition best suited for all purposes because these present varying physical and economic, as well as corrosive aspects. There is no single test now by which the usefulness of tin plate for all uses may be judged and it does not seem likely that such a test will be developed in the future. Quality evaluation of tin plate is a matter which can be considered only in respect to the ultimate use and such evaluation must be preceded by determining which of its many characteristics are important to the particular problem.

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Effect of Progress in Tin Plate Manufacture on the Use of Tin Plate for Cans for Foods[a]

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The requirements of products packed in metal containers vary widely. The ability of can manufacturers to produce the necessary cans with the minimum consumption of tin is shown to be primarily due to progress in the field of electrolytic tin plate production.

In a previous paper of this symposium, Meneilly *(6)* has outlined the progress which has taken place in the manufacuring procedures for tin plate. It will be the purpose in the following to indicate how the can manufacturing industry has been able to take advantage of improvements in tin plate manufacture either by producing a better container at no increase in cost or a satisfactory container at a lower cost. Particularly, it will be shown how the can manufacturing industry has been able to steadily increase the volume of metal containers manufactured and at the same time reduce the consumption of tin, a metal for which we are entirely dependent on foreign sources which on account of their distant locations and because of possible political disturbances may become inaccessible to us.

The plate requirements of cans for different products vary widely depending on the characteristics of the product and on the degree or nature of the protection required or desired in delivering the product to the ultimate consumer. In some cases the container is merely a convenient means of delivering the product to the consumer in a definite quantity and in a clean condition. In some instances the product may have no or practically no action on the plate as is the case with most dry materials such as coffee or powdered milk. In other instances the product may be relatively corrosive so far as foods go which is the case with canned soaked dried prunes and such other fruits as cherries and most of the berries. The degree of protection needed to prevent external rusting may vary widely depending upon the conditions under which the product is marketed or distributed. Plate for some products may have to be more resistant to high pressures than for others, such as that for the ends of beer cans or that for the ends of cans sterilized at high temperatures. For certain other cans such as drawn cans the plate must be quite ductile to prevent fracturing during the drawing operations.

For many of these classes of products one grade of plate could be used which would answer the requirements for all. For instance, tin plate with a heavy weight of tin coating and with the proper composition of the steel base plate could be used for products having a wide variation in their corrosive properties so long as this plate was suitable for the product of maximum corrosive properties. Such plate would also meet all requirements so far as external corrosion is concerned, but would result in an expensive container and a consumption of tin far beyond that justified by the availability of this metal.

In discussiong the subject of fitting the container to meet the requirements of the product, it should be pointed out that the tin plate manufacturing companies are not in a position to test their products from the standpoint of their ultimate use as containers. Therefore, changes in the manufacturing procedures for tin

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plate require extensive testing by the can companies in order to determine for what products the new or modified plate may be used. Such testing is one of the major expenses of can company research laboratories. The Continental Can Company, Inc., for instance, spends hundreds of thousands of dollars on such testing programs and other can company laboratories spend amounts of a similar order. Such expense has in the past been justified by the results obtained. The testing program starts with the plate and since as a rule a portion of the plate must be enameled, tests are made with all of the enamels used by the can manufacturer to determine whether the enamel will apply satisfactorily and has adequate adhesion. Soldering tests must be made to determine whether there is any surface film or other condition which will cause unsatisfactory soldering. Since there are no short cuts for determining the suitability of the plate for different products, particularly from the standpoint of internal corrosion, a variety of foods must be packed in cans made from the plate and subsequently stored and examined periodically over a period of time which in some cases may be several years. Changes in the internal vacuum of the cans during storage tests may be followed by "flip vacuum" determinations. It is only through such comprehensive testing that the can companies have been able to utilize to the greatest extent plate carrying the lighter weight of tin coatings applied by the electrolytic procedure. To provide information to meet emergency conditions caused by government restrictions on the use of tin, the research laboratories of the can companies have in the past pooled through the Can Manufacturers Institute research and testing results on the use of cans made from plate with the lighter weights of tin coating so that all existing data might be available to the entire industry. Such procedure has also enabled the can manufacturing industry to be of invaluable assistance to the government in the tin conservation program.

While no canned food is particularly corrosive in the sense that we frequently think of corrosion, practically all of them have some solvent action on tin plate, which, with many foods, will in the course of time result in the solution of enough iron to produce sufficient hydrogen gas to bulge the ends of the cans and render them unmerchantable. In rare instances the tin plate of the container may become perforated. While the pH of the product gives some indication of the relative corrosive properties of the food, this is not a true indication. However, it has become possible from many years experience roughly to classify most canned foods in this respect. This classification which is not new but is one which with some slight variation has been used in the canning industry for years, is as follows:

Class I Products. Those highly reactive to tin plate, such as berries (cranberries, loganberries, raspberries, and blueberries), cherries, and dried soaked prunes.

Class II Products. Those moderately reactive, such as peaches, pears, citrus fruits, etc.

Class III Products. Those relatively non-reactive, such as peas, corn, meats and fish.

This classification does not mean that the same type of plate is suitable for cans for all products in each group as there is some variation in the corrosive properties of individual products within each group.

Before the introduction of cold rolled plate, the cans which it was possible to make from hot-dipped tin plate were not very satisfactory from the standpoint of internal corrosion for Class I and also to some extent for Class II products. When tin plate from cold-rolled sheets became commercially available, about 1930, it was possible through control of the chemical composition of the steel *(2)* to make a can with a medium weight of tin coating which gave satisfactory results with Class I and Class II products. The cold rolling method of manufacture of steel sheets also permitted better control of temper and thickness thus providing a more uniform material for the manufacture of cans.

Class III products do not require cans made from plate carrying the minimum weight of hot dipped coating available previous to 1940. However, at that time the tin plate manufacturing industry did not consider it practical to apply hot-dipped coatings appreciably lower than 1.50 lbs. per base box and it was not therefore possible to adjust the weight of tin coating to meet the requirements of the mildly corrosive products.

At the beginning of World War II, tin conservation orders put in force by the government radically reduced the amount of tin which could be used by industry. The can manufacturing industry was forced either to find means of making containers by using less tin or substantially reducing the volume of containers manufactured. Although some reduction in volume was necessary, measures taken by the industry resulted very shortly in a material reduction in the amount of tin required. Fortunately some developments had already taken place which pointed the way.

In 1940 Colonel Paul P. Logan, then Major Logan of the Quartermaster Department, had been instrumental in calling a meeting of technical men connected with the canning industry and can manufacturing industry for the purpose of planning tests on the use of lower coating weights of tin on hot-dipped tin plate. The manufacture of hot-dipped tin plate having a coating weight of 1.25 lbs. of tin per base box instead of the previous minimum of approximately 1.50 lbs. per base box was considered commercially practical by the tin plate producing companies and tests carried out by the research laboratories of the can manufacturing industry in cooperation with the Research Laboratories of the N. C. A. with cans made of such plate showed that they were satisfactory for many products. In 1942 when a radical reduction in the use of tin was required by government regulations, a small amount of No. 50 electrolytic plate was being made and was being used mainly for coffee can ends and for a few other general line cans. Preliminary tests had indicated that it would be suitable for some of the less corrosive canned foods. Chemically treated black plate when coated with a suitable enamel, had also been found on preliminary tests to be satisfactory for the ends of cans for some of the less corrosive foods. Facilities for the manufacture of electrolytic plate of improved quality were rapidly installed. New low tin solders were developed to replace the 38% tin-62% lead solder most commonly used. These developments have been discussed elsewhere *(1, 3, 4, 5, 7)*. Government restrictions in the use of tin therefore accomplished in a short time changes which

most certainly would have taken place normally but would have required a period of years for their completion.

As tin became more available after World War II, government restrictions were relaxed but industry carried on in competitive efforts to produce suitable containers at a lower price. The use of electrolytic tin plate was extended. Previous to 1944 only No. 50 and No. 75 electrolytic tin plates were produced. In 1944 No. 25 electrolytic plate was first commercially produced and its use was rapidly extended to those products for which it was suitable. Coffee cans and other dry product cans were soon made entirely of No. 25 plate. Animal food cans were made of No. 25 plate as soon as government restrictions permitted the use of any tin plate for this product. Many non-food products such as paints, motor lubricating oil, anti-freeze, etc. were packed in cans made of No. 25 plate. In 1949 the Continental Can Company started to make beer cans of No. 25 plate to replace the No. 50 plate previously used. In 1950 a large percentage of the approximately 5,000,000,000 beer cans made by the industry were manufactured from No. 25 plate requiring the use of approximately 1100 long tons of tin out of a total of approximately 27,500 tons used in the form of tin plate by the can manufacturing industry in that year. The beer cans made previous to 1940 were manufactured from 1.50 plate which at the rate of production of such cans in 1950 would have required 6700 long tons of tin instead of the approximately 1100 tons actually used.

The manufacture of electrolytic plate made it possible to adjust the weight of tin coating to conform to the corrosive properties of many of the mildly corrosive products. The greater percent of the reduction in the use of tin has therefore been due to the use of electrolytic plate cans for such foods as meats, fish, and some of the large volume pack vegetables such as corn and peas. Its use for fruits is limited to the ends of cans for fruits such as peaches, pears, fruit cocktail, etc. where inside enameled electrolytic plate ends are used with plain inside hot dipped bodies. Such combination gives a service life or shelf life practically equivalent to that obtained when plain hot dipped plate throughout is used. This is illustrated in Table 1. The increase in the manufacture of electrolytic plate over the period 1942 to 1950 inclusive is shown in Table 2.

The data in Table 2 include plate used for cans as well as that for other purposes such as crowns. No distinction is made between the different electrolytic plates such as No. 25, No. 50, No. 75, etc., and no information for the entire industry is available on this point. However, some typical information on this subject is given in Table 3.

No. 75 plate is used only to a limited extent, less than 1% of the total, by the major can manufacturing companies. It is used to a considerably greater extent by those evaporated milk companies which manufacture their own cans and its use has been increased in 1951 by N. P. A. Order M-25 because of being specified for the ends of 14-½ oz. milk cans. The use of No. 25 plate has been gradually increasing over the last four or five years replacing No. 50 plate for a number of products. The greatest use in 1950 was for such products as beer, coffee, and animal foods; and in the non-food field for motor lubricating oil cans, anti-freeze cans, and paint cans. In 1951 the use of No. 25 plate in comparison with other weights of coating will increase considerably above 1950 due to its much wider specification in N. P. A. Order M-25. Since in many instances it is being used as a replacement for No. 50 plate, the use of the latter will decrease correspondingly. The result will be a further reduction in the average weight of tin coating on plate used for cans both food and non-food. Table 4 gives the calculated average tin coating weight in terms of pounds of tin per base box of the tin plate produced over a number of years.

TABLE 1

Effect of varying tin coating weight of ends on rate of formation of hydrogen springers in canned apricots and canned peaches

Product	Coating weights of tin plates used		Time for 25% hydrogen springers at 98° F. storage
	Bodies	Ends [b]	
Apricots	1.50	1.50	19 mos.
	1.50	0.50	25 mos.
	1.50	0.10	23 mos.
Peaches	1.50	1.50	30 mos.
	1.50	0.50	30 mos.
	1.50	0.25	27 mos.
	1.50	0.10	27 mos.

[b] With the exception of 1.50 plate, all ends were inside enameled, all bodies were plain inside.

TABLE 2

Electrolytic tin plate and hot-dipped tin plate production from 1942 to 1950 [a]

Year	Hot Dipped	Electrolytic
	%	%
1942	97.0	3.0
1943	84.7	15.3
1944	75.6	24.4
1945	69.1	30.9
1946	66.9	33.1
1947	52.8	47.2
1948	51.2	48.8
1949	45.8	54.2
1950	40.2	59.8

[a] Calculated from production figures furnished by the American Iron and Steel Institute.

TABLE 3

Electrolytic and hot dipped tin plate used in can manufacture, 1947-1950

Year	Hot-Dipped (1.50 and 1.25)	Electrolytic		
		No. 75	No. 50	No. 25
	%	%	%	%
1947	47.6	0.5	35.2	16.8
1948	43.5	0.6	33.0	22.8
1949	38.7	0.4	25.4	35.4
1950	35.9	0.2	23.3	40.6

TABLE 4

Average weight of tin coating per base box of tin plate produced in the United States 1940-1950

1940	1.50 lbs. per base box
1941	1.36 lbs. per base box
1942	1.10 lbs. per base box
1943	1.05 lbs. per base box
1944	0.99 lbs. per base box
1945	0.97 lbs. per base box
1946	1.00 lbs. per base box
1947	0.86 lbs. per base box
1948	0.83 lbs. per base box
1949	0.83 lbs. per base box
1950	0.81 lbs. per base box

The above figures are only approximate since there is no accurate data on the total tin used in the manufacture of tin plate in the United States. Actually, the figures given for recent years are slightly too high for tin plate used in the manufacture of cans in the United States. They are based on the total production which includes export plate, the greater percentage of which has been hot dipped. Coating weights calculated from Continental Can Company tin plate orders show averages below the above for recent years, and it is believed that those for other major can companies would show a similar trend. The percentage of tin coating reduction since 1940 on tin plate for cans for various products has naturally varied depending on the corrosive properties of the product. In Table 5 is given the percentage reduction for some of the larger volume products as of 1950 and also as of 1951, the latter being based on N. P. A. Order M-25, April 6, 1951.

TABLE 5

Percentage reduction in tin coating since 1940 for some of the larger volume products

Product	Percent reduction in tin coating	
	As of Dec. 31, 1950	As of April 6, 1951
	%	%
Cherries, berries	11.8 [d]	11.8 [d]
Peaches, pears, fruit cocktail	26.9 [e]	36.9 [e]
Animal foods	83.3 [g]	83.3 [g]
Potted meat and some other meat products	66.7 [g]	83.3 [g]
Corn, peas, shelled beans	66.7 [g]	83.3 [g]
Tomatoes	35.6 [g]	41.9 [g]
Tuna	66.7 [g]	83.3 [g]
Evaporated milk, 14½ oz. can	16.3 [g]	28.3 [g]
Coffee cans, vacuum pack	83.3 [g]	100.0 [f]

[d] Based on 1.70 pot yield tin coating throughout in 1940.
[e] Based on No. 2½ cans and 1.50 pot yield tin coating throughout in 1940.
[f] Black plate specified in M-25.
[g] Based on use 1.50 throughout in 1940.

In the case of evaporated milk cans, because of the style of can used, it has not been possible to make a tin reduction commensurate with the corrosive properties or rather lack of corrosive properties of the product which would place it in the same class as corn or peas and should make it possible to use a can made of No. 25 plate throughout.

Electrolytic tin plate carrying the lower weights of tin coating such as No. 25 and No. 50, when used in whole or in part for cans for foods containing appreciable quantities of moisture must, in most instances, be inside enameled to give maximum corrosion resistance. Even for cans for mildly corrosive products it is desirable to use an inside enamel as illustrated by the data in Table 6 giving the comparative rates of corrosion of plain No. 50 and inside enameled No. 50 electrolytic plate cans packed in one instance with dog food and in the other with fresh peas.

TABLE 6

Effect on rate of interior corrosion of inside enameling No. 50 electrolytic plate cans

Product	Cans inside enameled	Hydrogen springers when stored at 98° F.
Dog Food	No	100% at 18 months
Dog Food	Yes	None at 36 months
Peas	No	25% at 22 months
Peas	Yes	3% at 48 months

While in one respect the necessity of inside enameling of electrolytic plate cans is a disadvantage in that it slightly increases the cost of the container and increases considerably the equipment investment of the can manufacturer, it has had one desirable advantage. Most of the sterilized canned foods which may be satisfactorily packed in cans made entirely of electrolytic plate are of a type which on account of the liberation of sulphur compounds during sterilization, discolor the interior of plain cans. The fact that the can had to be inside enameled to increase corrosion resistance has therefore had the additional advantage of eliminating such discoloration therefore producing a more attractive interior appearance. This has eliminated complaints of discoloration from consumers which sometimes occurred when plain inside cans were used for these products.

However, the necessity of inside enameling has made it difficult to reduce the consumption of tin for evaporated milk cans to the degree that its characteristics of the product should permit. This is the only large volume product for which cans with soldered end seams are used and this type of can is somewhat difficult to manufacture from enameled plate. In addition, such cans are made largely by evaporated milk companies who do not now have facilities for enameling tin plate.

Special enameling procedures made it possible to use No. 25 plate for beer cans and further developments in enameling procedures may make it possible to use plate with lower weights of tin coating for products such as berries and cherries where 1.50 plate is now used.

The question may arise as to the permanency of the specifications for plate for cans in N. P. A. order M-25 issued in 1951 in view of the fact that these specifications are based on the necessity of conservation of tin beyond that contemplated by industry in the normal manufacture of containers. Insofar as these containers meet the needs of users and insofar as at the same time they represent an economical advantage over containers previously used for the products in question they may be regarded as permanent changes. In some instances where it is necessary to use an outside enamel over No. 25 plate for additional protection and where plain outside No. 50 plain was previously used, what will be used after the present emergency has passed will depend on the comparative costs of tin and enameling. Where black plate has been substituted for No. 25 tin plate as in the case of certain dry products, here also future use after the emergency has passed will depend on the comparative cost of plain tin plate and enameled black plate. In some instances manufacturing difficulties may also be a factor in changing from black plate back to tin plate. Regardless of what changes the future may bring, it will have been beneficial both to the can manufacturing industry and to the user to have had an experience which has forced the use of the minimum amount of tin. In the case of a country situated as is the United States with no known domestic tin sources, it is desirable to know how to make suitable containers with the minimum of tin even though in normal times it may

be more economical to make them by using more than that minimum.

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Record of Discussion Which Followed the Presentation of the Four Papers in the "Panel on Tin Plate for Food Containers"

JOHN T. KNOWLES, Presiding

Mr. Knowles: You have just heard four carefully selected experts in the field represented by the titles presented . You now have the opportunity of asking questions.

Question: What weight of tin coating is used on export plate?

Mr. Meneilly: Export tin plate has generally carried a heavier tin coating weight than domestic tin plate. For a variety of reasons can manufacturers in other countries have not employed as great a percentage of electrolytic plate as is utilized in this country. Last year 17% of the export plate was electrolytic as compared with 60% of the plate consumed in this country. However, this situation is changing very rapidly. In the first quarter of this year, 35% of all plate exported was electrolytic and we expect that the figure for the entire year will be approximately 40%.

Question: Is it probable that new developments will produce No. 25 or No. 50 electrolytic plate that can be used without enamel?

Mr. Hartwell: No. Most of us who have had experience with these plates think that it is unlikely that No. 25 or No. 50 plates will be used for processed food products without enameling. We do think, however, that the corrosion resistance of heavier electrolytic coatings can be improved to the point where these plain plates may be substituted for many items where hot dipped plate is now used.

Question: I would like to ask Mr. Stevenson if plastics can be substituted for tin.

Mr. Stevenson: As far as I know, very little progress has been made in attempting to substitute plastics for tin plate. I know of no plastic which is suitable for processed food products.

Question: I wonder if Mr. Stevenson has any data to present concerning the performance of plain No. 75 electrolytic bodies as compared with plain hot dipped bodies.

Mr. Stevenson: We have comparison data, but I do not have it with me. The plain No. 75 electrolytic bodies, however, have not given as long a shelf life as plain hot dipped bodies.

Question: Can it be definitely said that there are no tin ore deposits of commercial significance in the United States?

Mr. Meneilly: Yes. Last year a small tonnage was mined in Alaska and minor deposits have been discovered in the southern part of the United States, but none of these can be considered commercially significant.

Question: Is it necessary, Mr. Stevenson, to outside enamel No. 25 plate such as the N. P. A. order specifies for some processed food products?

Mr. Stevenson: I don't think I can answer that by categorically saying yes or no. Plain No. 25 plate has been used for animal food cans for about five years without any major difficulties. In fact I have heard no complaints. However, in view of the fact that we have no information on other processed foods, the Research Committee of the Can Manufacturers Institute recommended that the ends be outside enameled until more information, or experience, can be obtained.

Question: Mr. Hartwell, I understand that when the electro deposit of tin is melted, agglomeration takes place. Although the tin coating weight is very uniform on a macro scale, there may be major differences in thickness on the micro scale. If this is true, will it ever be possible for these electrolytic plates bearing thinner tin coatings to take the place of hot dipped plate?

Mr. Hartwell: I agree that some agglomeration takes place and that there are holes in the coating down to the steel, probably more of them in melted electrolytic plate than in plate with a matte finish. However, I think that a plain electrolytic tin plate can be developed which will provide a service life approaching very closely that which is now being obtained from plain hot dipped plate on many canned food items. Experimental ways of increasing the corrosion resistance on plain electrolytic plates are now fairly well known. The main problem is

one of finding some practical, and that means economical, way to overcome the difficulties that we think are responsible for poor corrosion resistance.

Question: Mr. Stevenson, you mentioned that when combination cans with enameled ends and plain hot dipped bodies are used, the tin ions protect the ends against corrosion. I think that a bigger factor is the electrolytic protection of the enameled ends by the plain bodies.

Mr. Stevenson: I don't know whether it is a bigger factor or not, but I will agree that there is probably some electrochemical protective effect.

Question: What is the basis for determining the shelf life required for any product?

Mr. Hartwell: Our judgment on the shelf life required is based on the time which has been established by commercial practice as providing a reasonable margin of safety for the individual product being considered.

Question: What operation in the manufacture of tin plate do you think is responsible for the difference in the corrosion resistance of plain electrolytic and hot dipped plates?

Mr. Hartwell: The pickling and fluxing of hot dipped plate are quite different than that of electrolytic plate. We think that the corrosion resistance of electrolytic plate would be benefited if some procedure were developed which would perform the same function as does the pickling and fluxing of hot dipped plate.

Question: Has any progress been made in continuously hot dipping plate?

Mr. Meneilly: Some continuously hot dipped plate has been produced in Germany on strips less than 20" wide. That is entirely too narrow for use in the United States. We have recently made another attempt to hot dip plate continuously but are beginning to think that the operation is not economically sound.

Question: Dr. Martin, what is the commercial variation in the weight of tin plate in terms of pounds per base box?

Dr. Martin: The present tolerance for individual sheets is plus or minus 10%. Considerable progress has been made in reducing the variation in weight within any one shipment. I think that today you would find that 85% of the individual sheets are within 5% of ideal.

Question: Mr. Hartwell, can aluminum be substituted for tin plate?

Mr. Hartwell: Aluminum can and is being used for a few products, particularly in the Scandinavian countries where the cost factors are more favorable. It is unlikely that any significant quanties of aluminum can be substituted for tin plate in the United States because of cost factors as well as difficulties of application due to physical and chemical characteristics of aluminum.

Question: What is the average tin coating weight on cans made of standard coke plate and how many cans should be tested to obtain this average weight?

Dr. Martin: The tin coating weight test values shown in Table 2 of my paper are the minima which one may expect to encounter when the plate is tested according to the procedure recommended under "Sampling." Experience has shown that the average tin coating is substantially higher than these values; for example, production control test records indicate that over an extended period, the average coatings on common cokes and standard cokes will approach 1.10 pounds per base box and 1.35 pounds per base box respectively. Statistical analyses of these data indicate that approximately 2,000 samples are required to approach the true average. From this, it is obvious that a few samples taken from a carload of cans will not provide reliable information regarding their average coating weight.

Question: Mr. Meneilly, do the tin coating figures which you presented mean that a single sample cut from a can made from standard coke plate may have a tin coating weight as low as 0.8 lb. of tin per base box?

Mr. Meneilly: My answer is yes, and perhaps occasionally lower than that.

Question: Mr. Stevenson, your data showed fairly good results for certain fruit cans with ends having a tin coating weight lower than that specified by tin conservation order M 25. Could these lighter weights be used commercially with any success?

Mr. Stevenson: We think they can. As an example, we think enameled No. 25 ends could be used on peach cans, but we would prefer to see semi-commercial packs made before No. 25 plate is adopted on a universal scale.

Question: Mr. Hartwell, you mentioned that a small amount of chromium in the steel base is not beneficial as far as corrosion resistance is concerned. Is there any explanation for this, as it would seem that the addition of chromium would increase resistance?

Mr. Hartwell: I can not give you a precise answer because it is not known whether this effect of traces of chromium results from a change in the nature of the steel as a whole or merely of the base metal surface. It should be emphasized however, that the chromium normally present in tin plate steel has no significant influence on service life for the large majority of tin plate uses.

Question: We have been talking about what food does to the can. Let's talk now about what the can does to food. Which will impart tin to the food more rapidly—hot dipped or electrolytic plate?

Mr. Hartwell: At the present time electrolytic coatings are generally corroded more rapidly than hot dipped, but we have results where the opposite is true. We think, however, that the time will come in the not too distant future when the rate of corrosion will be essentially the same.

Instruments for Objective Measurement of Quality Control Factors in Processed Food Products[a]

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Instruments needed for measuring quality control factors of processed foods are enumerated and their importance is discussed. The qualifications necessary for such instruments to be applicable and useful are given.

In the last ten years, quality control of food products has been a favorite theme for discussion at meetings of the IFT or other professional associations, and has been the subject of many publications by university workers and industrial scientists in trade journals and elsewhere.

From the point of view of the manufacturer of processed food products, many of these discussions have concerned themselves primarily with quality inspection or recording, and not with real quality control.

By quality control, we mean control of quality of a food product as far back as practicable in the growing, handling, or manufacturing processes, which embraces control of the materials, methods, equipment, and personnel involved insofar as factors affecting quality are concerned. The inspection of the finished processed product is, of course, an essential part of any quality control problems than straightforward canning operathis stage, it is often too late to exercise effective quality control. If we can exercise real quality control in the early stages of the process, then our final quality inspection should be more or less routine and mostly for confirmation of past control and for recording results as guidance for future control *(2)*.

It should also be pointed out that this discussion deals primarily with manufactured or compounded food products, most of which contain many different materials and are subjected to a variety of manufacturing processes, and therefore usually present more complex control problems than straightforward canning operations of fruits and vegetables.

To borrow a medical metaphor, quality control should emphasize "preventive" features, and not concern itself primarily with post mortem examinations or with "diagnosis" of production problems. If we keep this concept in mind, it will be realized that although there are many sensitive and satisfactory instruments available for research on quality factors in foods and for the inspection and recording of the quality of processed and packaged foods, we are not nearly so well provided for in the field of instruments for quality control as we define it.

By the nature of things, preventive quality control must be carried out to a considerable extent in the receiving department or in the factory. For many inspections we depend upon what the eye can see, what the finger and thumb can feel, or what the nose can smell. It would be most helpful to have suitable instruments for this purpose or for use at an early stage of the process. Such instruments need not be as accurate or precise as those used for quality research, but must be simple in operation, rugged in construction, and comparatively inexpensive in price.

Most of the instruments available for measuring objectively what are in effect organoleptic factors, are apparently designed primarily as research tools, and of course industry owes a debt of gratitude to research workers in this field who have created a demand for the development of the equipment now available and to the instrument makers who have developed the tools involved. However, I believe the time has come when there should be sufficient interest in preventive quality control to justify the development of modified instruments to function in this particular field.

Some instruments are at present available which fulfill practically all the requirements for a quality control instrument, and a brief discussion of these will serve to emphasize the requirements to be met in other fields of quality control. The discussion of these instruments is based on personal experience and observation on products or processes with which I am familiar at Crosse and Blackwell and elsewhere, and no doubt the list of suitable and unsuitable instruments can be extended by every food technologist, based on his own experience with other products.

In our experience the refractometer is an outstanding example of a satisfactory quality control instrument. We use refractometers for determining the end point of evaporation of preserves and jellies *(10)*, for controlling the sweetening process of pickles and candied peel, and for control tests on many other products. "Abbe type" refractometers are now constructed so that even when dozens of readings are made daily, sometimes under adverse atmospheric conditions, many months will elapse before repairs are needed. Apart from its high price, the chief criticism of the Abbe type refractometer is the difficulty of obtaining a satisfactory reading with dark-colored products or with products which have insoluble solids present. These objections are largely overcome by a new reflection type instrument now available, and are not so pronounced with the pocket refractometer which is useful in control operations where strict accuracy is not required.

Another quality control operation which is well provided for by instrument manufacturers is the determination of pH. We all know the importance of controlling this factor in many operations such as determining the

[a] Presented at the Eleventh Annual Meeting of the IFT, New York, N. Y., June 19, 1951.

jellying properties of fruit juices *(15)* or determining heat process requirements, and the pH reading can also be used as a check on uniformity of many mixing or manufacturing operations. Modern pH meters operating from the electric circuit are quite accurate for control purposes, and with the minimum of precaution in operation have a comparatively long life, and do not need trained scientists or other experts to operate them. A word of warning is in order here, so that in our enthusiasm for pH readings, we do not overlook that basic control factor, the titratable acidity. This factor is particularly important for products such as sweet pickles and tomato catsup which depend in part on the vinegar or acetic acid content for proper preservation. Here the titratable acidity, confirmed by determinations of the volatile acidity, is a much better guide for the acetic acid content than is the pH reading. Even with preserves, jellies, and fruit juices, the titratable acidity is a better guide to the acid component of the flavor than the pH reading.

In other measurements of quality factors the food technologist interested in preventive quality control of processed food products is not so well provided with acceptable instruments, particularly in measurements of texture and consistency. In our own operations, we are not satisfied with the consistency or viscosity measurements now available for non-homogenous products such as tomato catsup. For this important characteristic of tomato catsup there is no general agreement among food technologists as to what instruments should be used for recording the consistency of the finished product. Still less agreement exists as to what measurements can be made on the tomato juice used or on the catsup itself during evaporation to predict the final consistency which will be obtained in the bottled catsup, but that is just what we would like to be able to do for real quality control.

One of the most widely used instruments for measuring the final consistency of catsup is the Bostwick consistometer, which is the instrument specified for this purpose in the U. S. D. A. grades for catsup *(14)*. Manufacturers who sell catsup to the armed services or other government agencies must know the Bostwick reading of the catsup they offer, as well as any readings they make with their own favorite instrument. There are a number of objections to the Bostwick consistometer as an instrument for recording catsup consistency. For example, there is not enough spread in readings between a very thick and a moderately thick consistency and if many readings are made, as is necessary in control work, it is difficult to obtain reproducible results. In addition, some parts of the instrument have a short life. Many catsup manufacturers have devised some type of "funnel" viscosimeters for their own control procedures, which are more sensitive in the readings obtained than the Bostwick consistometer and give results better correlated with the way the catsup flows from the bottle. In addition to this flow factor of catsup, the "spread" on a plate after pouring from the bottle is important to the consumer. There is considerable interest recently in various types of "spreadmeters" which might be adapted to catsup and similar products. Here a measurement is made of the area covered by a given volume of catsup which has been allowed to spread on a flat surface for a given length of time. The N. P. A. spreadmeter *(11)*, the Tuc corn meter, and the Adams corn consistometer are in this category. Other scientific instruments have been also used in research on catsup such as the Stormer viscometer and the Brookfield synchrolectric viscometer *(3)*, both being quite promising for quality control work, due to the comparative simplicity in construction and operation accompanied by a reasonably low price.

Even when agreement is reached as to the best equipment to use for measuring consistency, there still will be the real quality control problem of predicting the final consistency from the raw materials used or from the product in process. Effective solution of these questions will require cooperative work by food processors and instrument makers.

We have another consistency problem with jellies and preserves. The best method of determining the jelly strength of pectin jellies has been the subject of voluminous publications and discussions in connection with the standardization of the grading of manufactured pectin, and the IFT has had a committee working on this problem for several years in conjunction with the N. P. A. and the pectin manufacturers. There is still some disagreement as to whether some form of the "sag" test such as ridgelimeter of the California Fruit Growers Exchange *(5)* is all that is needed, or whether some modification of the breaking strength method of the Tarr-Baker type *(16)* is also required as a method of measuring the "strength" of the pectin as far as its sugar holding or jellying capacity is concerned *(13)*.

For the manufacturer of fruit jellies this problem of jelly strength is rather more complicated, as we must consider which method of determination will best describe the properties desired in our jellies. Two of these properties are the ability of the jelly to stand "agitation" during shipment, and the ease of spreading when received by the customer. Therefore our requirements are not necessarily the same as those of the pectin manufacturers. Any standard method for measuring the strength of the jelly will give us some form of quality inspection, but to develop methods for real control more research is needed. A viscosity test or some other form of determination performed on the mixture of fruit juice, sugar, and pectin, might predict the final characteristics of the jelly produced.

Another inspection and control problem which presents some interesting possibilities is the consistency of processed soups, particularly those containing cornstarch and other cereal thickeners. There is no recognized method for measuring this consistency in the finished soup, although methods used in starch and flour laboratories such as the Dudley pipette, and the Scott test have been suggested as well as viscosity measuring instruments such as the Stormer and Brookfield viscometers or the FMC consistometer. Yet, even when an inspection method has been agreed upon for quality control, we will still need a test which can be made on the cooked soup before canning. This test should correlate with the consistency after canning, so that we can

vary our ingredients if necessary to obtain a uniform processed product to compensate for the changes in consistency which take place when cereal suspensions are heated to 240° or 250° F. in the presence of vegetables or other ingredients.

The texture of fruits and vegetables is a very important factor from the point of view of the consumer, and offers a challenge to the food technologist and the instrument manufacturer to find a satisfactory method of recording or measuring this characteristic. Such measurements have been the subject of considerable research at the University of Maryland and elsewhere.

Considerable progress has been made with vegetables where various special purpose instruments have been widely adopted, such as the Tenderometer for measuring the tenderness of peas *(6)*, and the Succulometer for measuring the tenderness of corn *(9)*. With cucumbers and apples the use of the Magness-Taylor pressure tester of the U. S. D. A. *(4)* has been recommended and other instruments have also been suggested for measuring the toughness or fibrosity of asparagus and the texture of apples or peaches. None of these has yet been generally accepted as entirely satisfactory by the canning or preserving industries. A recent development in this field is the "shear-press" instrument of the University of Maryland *(8)* which is designed to be a multi-purpose instrument for measuring the texture of various vegetables and fruits before and after processing, but it remains to be seen if this instrument will fulfill all expectations.

The question of the measurement of the texture of fruits in order to judge their suitability for use in freezing or canning or preserving has so far received very little quantitative study. This is a particularly difficult problem due to the variation in texture of individual slices from the same fruit as with apples or peaches, and on acount of the variation between the texture of individual fruits such as cherries and strawberries from the same container *(1)*. Perhaps this problem should not be more difficult than the variations between individual peas from the same pod, so presumably if there is enough demand and enough cooperative work, fruit processors should be able to obtain "texturemeters" for various fruits which will be as useful as the Tenderometer has proved to be for the canners and freezers of peas.

For color measurement or color recording of the finished product, there appears to be a number of satisfactory instruments to choose from. These range from expensive spectrophotometers to comparatively simple colorimeters which are in effect quantitative Nessler tubes. One difficulty with many methods of color measurement for food products is that the color measured or recorded is only that of the absorption or refiection of the dominant wave length and does not always give the whole color effect as seen by the consumer *(12)*. With some products such as asparagus and peaches the pigments extracted by a solvent and measured by a suitable instrument has been found to be a good expression of the color as observed visually. With other products such as tomato juice and preserves we need, in addition, color properties of chroma and value to obtain a color reading which will be equivalent to that observed by our eyes. The Hunter color meter appears to be a most promising instrument for this purpose, and has received intensive study for the last couple of years in work on tomatoes and tomato products, where it seems to give very satisfactory results *(7)*. Although this instrument has the big advantage of being simple to operate, its high price will presumably prevent widespread adoption for control work. No doubt in the normal course of evolution and competition, we will have simplified forms available which will give similar results sufficiently accurate for control or inspection purposes, and yet priced to be more within the means of the average food products manufacturer. A recent development in this field is the "Agtron" photoelectric reflectance equipment recently adopted in California for the inspection of raw tomatoes for grading purposes.

This brief review of some of the unsolved problems in the field of instruments for objective tests of quality control factors indicates a need for a concerted attack on the problem by instrument manufacturers and prospective users. There would seem to be an opportunity for the Institute of Food Technologists to function as a coordinating organization to stimulate and correlate this cooperative work. A committee to study objective methods for measuring quality control factors could investigate the problems involved, and develop standard equipment and methods of procedure along the lines of the A. S. T. M. Such a committee, I believe, would command the support of the instrument manufacturers as well as all members of the food products industry interested in the objective measurement of quality factors.

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Browning of Dehydrated Sulfited Vegetables During Storage[a]

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Correlation has been made of the effects of moisture content, sulfite, package atmosphere, and storage temperature on browning of dehydrated white potato, carrot, and cabbage. Substantial protection against browning is afforded by low moisture and also by sulfite. Decrease in rate of browning per 2% decrease in moisture content was found to vary from 1.2- to 4.6-fold, depending on kind of vegetable and moisture content. The moisture effect increased as the product approached complete dryness. Rates of browning increased 6- to 8-fold per 18° F. (10° C.) rise in temperature. There was little difference in rate of browning of air- and nitrogen-packed samples.

In connection with the current program of procurement of dehydrated vegetables for the armed forces, need has arisen for information on factors that affect initial quality and storage stability of the product. In particular, there is need for data relating properties of dehydrated vegetables with their behavior in storage at elevated temperatures. It is generally considered that under these conditions, nonenzymatic browning is the principal deteriorative process.

Numerous articles *(2, 4, 7, 8, 15)* have appeared on nonenzymatic browning of dehydrated vegetables. For purpose of simplification the nonenzymatic browning process will be referred to hereinafter as "browning." It is known that the rate of browning is accelerated by increasing temperature and moisture content, in the range ordinarily encountered with dehydrated vegetables. Some data have been obtained on the relation between composition of product and browning tendency. For example, it has been reported that browning tendency of dehydrated white potato is roughly proportional to its reducing sugar content *(1, 3, 5, 6)*. There is some evidence also of a rough relationship between browning tendency and amino nitrogen content *(2)* of the dehydrated white potato.

This paper is concerned primarily with quantitative evaluation of browning rate of dehydrated sulfited white potato, carrot, and cabbage as a function of moisture content, sulfite, package atmosphere, and storage temperature. The results reported are a part of those obtained from an extensive investigation undertaken during World War II. Certain phases of this investigation have been reported in previous articles dealing respectively with browning of nonsulfited dehydrated vegetables *(12)*, sulfite disappearance in dehydrated sulfited vegetables *(13)*, and preliminary findings with regard to in-package desiccation *(10, 11)*. Succeeding articles will deal with gas changes and vitamin retention during storage, in-package desiccation, and vapor pressure-moisture relations.

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[b] U. S. Department of Agriculture, Agricultural Research Administration, Bureau of Agricultural and Industrial Chemistry.

EXPERIMENTAL

Preparation of materials. Details pertaining to experimental materials are shown in Table 1. All of the dehydrated sulfited vegetables were adequately blanched on the basis of enzyme tests specified by the U. S. Army Quartermaster Corps *(20)*. Samples for storage tests were usually packed in sanitary tinned cans: size 211 x 413 for carrot and potato, and 401 x 411 for cabbage. A definite amount of dried vegetable was placed in each can: 125 g. of carrot and potato, 130 g. of cabbage. The cans were closed with a semiautomatic double seamer.

TABLE 1

General information and analytical data on dried vegetables used for storage studies

Commodity[c]	Lot no.	Sugar as glucose (M.F.B.), %[d]		Moisture (M.F.B.)	Sulfur dioxide (M.F.B.)	Optical density of extract[e]
		Total	Reducing			
		%	%	%	*p.p.m.*	
White potato	1[f]	4.9	2.2	9.2	340	0.110
		4.9	2.2	7.6	330	0.105
		4.9	2.2	5.3	340	0.110
		4.9	2.2	8.9	0	0.135
		4.9	2.2	7.6	0	0.140
		4.9	2.2	5.3	0	0.148
	2	2.6	1.4	8.0	400	0.104
		2.2	1.3	8.0	0	0.144
	8	3.1	1.2	8.6	220	0.120
		3.1	1.2	5.0	220	0.120
	9	3.6	1.4	7.0	600	0.104
		3.6	1.4	4.8	600	0.104
	10	1.9	0.8	7.5	500	0.122
		1.9	0.8	5.1	500	0.122
	11	2.9	1.3	8.8	260	0.152
		2.9	1.3	5.1	260	0.152
	12	2.6	1.1	7.7	670	0.120
		2.6	1.1	5.0	670	0.120
Carrot	1[f]	57.5	16.3	8.0	2190	0.024
		57.5	16.3	6.2	1920	0.026
		57.5	16.3	5.4	1740	0.028
		61.8	17.3	8.0	0	0.045
		61.8	17.3	6.2	0	0.050
		61.8	17.3	5.4	0	0.060
Cabbage	2	49.3	8.0	6.0	660	0.090
		49.5	10.5	6.0	0	0.166
	1	....	....	7.1	940	0.080
		....	....	3.5	1000	0.070
		....	....	2.1	1080	0.090
	2	48.4	47.0	3.2	930	0.111

[c] All white potato lots and carrot lot 1 were in form of half-dice (⅜ x ⅜ x 3/16 inch before dehydration); carrot lot 2 was full dice; cabbage was in form of shreds.

[d] M.F.B. indicates moisture-free basis.

[e] White potato, $E^{5\%}_{2\text{ cm.}, 390\ m\mu}$; carrot, $E^{2\frac{1}{2}\%}_{1\text{ cm.}, 420\ m\mu}$; cabbage, $E^{2\frac{1}{2}\%}_{2\text{ cm.}, 420\ m\mu}$.

[f] Processed in the pilot plant of the Western Regional Research Laboratory. Other dried commodities were from commercial plants.

In this paper, "nitrogen pack" means oxygen content of 1.5 ± 0.5% in the atmosphere of the freshly packed can. The method used for effecting a nitrogen pack is described in a previous paper of this series *(12)*. All samples from storage, whether air- or nitrogen-packed, were analyzed for oxygen and

carbon dioxide content of their atmospheres immediately before other tests were conducted on the samples. Whenever results of gas analyses indicated leakage of the container, the data for the involved sample were discarded.

Moisture, sugar, and sulfite determinations. The moisture contents of the dried vegetables were determined according to the method of Makower, Chastain, and Nielsen *(14)*. The method involves grinding the sample to pass a U. S. Standard 40-mesh sieve and drying in a vacuum at a total pressure of less than 5 mm. of mercury. Oven temperatures (shelf) and drying times used were 60° C. and 30 hours for cabbage and 70° C. and 40 hours for carrot and potato. It is to be noted that this method (with exception of cabbage and onion) yields moisture values considerably higher (about 1.5 to 2%, absolute) than those obtained by the so-called 6-hour method described in the Tentative Specifications of the U. S. Army Quartermaster Corps *(20)*. Differences in values obtained by these two methods depend on a number of factors. For discussion of this subject, the reader is referred to the original articles of Makower et al. *(14, 15, 16)*.

Sulfite determinations were made according to the method of Prater, Johnson, Pool, and Mackinney *(18)*. Data and generalizations regarding rate of sulfite disappearance in the samples were reported in a previous communication *(13)*.

Sugars were determined by the method outlined in the Fruit and Vegetable Dehydration Manual *(21)*.

Estimation of brown color. The "brown" color formed in samples during storage was measured by the method of Hendel, Bailey, and Taylor *(9)*. In essence, the method consists of measurement of the transmissivity of a clear extract of the dried vegetable. The precision of measurements on potato, onion, carrot, cabbage, and sweet potato has been reported *(12)*. Results of the so-called water soluble (brown) color measurements are expressed as optical density (log I_o/I). In referring to optical density, the symbol E is used with a superscript and two subscripts which represent, respectively, the extract concentration, cell length, and the color filter used. Thus $E^{5\%}_{2\text{ cm.},\ 390\ m\mu}$ refers to the optical density of an extract prepared on the basis of 5 g. of material per 100 ml. of solvent, with transmittance measured with a photoelectric colorimeter equipped with a 2-cm. cell and a color filter with a maximum transmittance at 390 mμ.

Treatment of data. Results of the various storage experiments have been expressed as time intervals required for development of three respective degrees of browning. The lowest degree (Low) is in the neighborhood of a barely visible change (in appearance of the cooked product). The highest degree (High) represents 5 times as much browning, on the basis of "soluble color" measurement. This would correspond roughly to the "limit of palatability," defined in a previous paper *(12)*. The other level (Medium) of browning is mid-way between Low and High.

The values tabulated in Tables 2 to 4, were read from plots of optical density versus time as shown in Figure 1. These

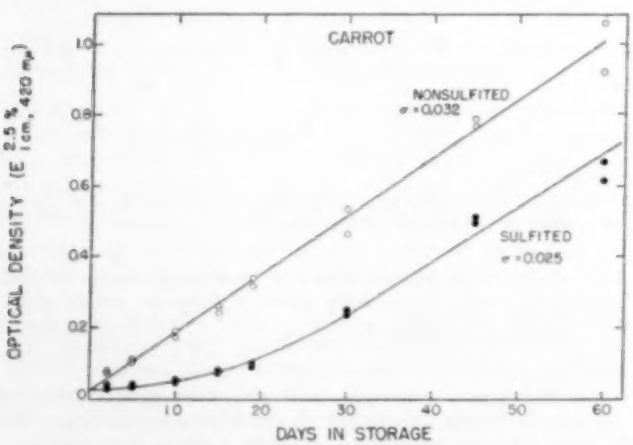

FIGURE 1. Course of browning of dried carrot (Lot 1) stored at 100° F. (38° C.). Moisture content (M.F.B.), 6.2%; Initial SO_2 content of sulfited sample, 1920 p.p.m.

TABLE 2

Effects of moisture, atmosphere, and temperature on browning of dehydrated sulfited white potato. (Lot 1, initial sulfur dioxide content: 330 p.p.m.)

Storage temp.	Atmosphere	Moisture (M.F.B.)	Days required for various degrees[a] of browning		
			Low	Medium	High
° F.		%			
120° (49° C.)	Nitrogen	9.2	5.4	11	15
	Nitrogen	7.6	7.8	15	20
	Nitrogen	5.3	17	32	45
	Air	7.6	7.3	14	17
110° (43° C.)	Nitrogen	9.2	13	27	37
	Nitrogen	7.6	21	44	61
	Nitrogen	5.3	42	>61	>61
	Air	7.6	19	40	58
100° (38° C.)	Nitrogen	9.2	38	84	115
	Nitrogen	7.6	78	140	185
	Nitrogen	5.3	200	>365	460
	Air	7.6	66	125	162
90° (32° C.)	Nitrogen	9.2	108	200	270
	Nitrogen	7.6	190	320	410
	Nitrogen	5.3	490	>600	>826
	Air	7.6	96	230	330
75° (24° C.)	Nitrogen	9.2	450	650	>826
	Nitrogen	7.6	730	>820	>826
	Nitrogen	5.3	>826	>690	>826
	Air	7.6	420	>690	>826

[a] Low, medium, and high represent changes in optical density $\left(\Delta E^{5\%}_{2\text{ cm.},\ 390\ m\mu}\right)$ of 35, 105, and 175 x 10^{-3} units, respectively.

TABLE 3

Effects of moisture, atmosphere, and temperature on browning of dehydrated sulfited carrot

Storage temp.	Atmosphere	Moisture (M.F.B.)	Days required for various degrees[b] of browning		
			Low	Medium	High
Lot 1, initial sulfur dioxide content: 1920 p.p.m.					
° F.		%			
120° (49° C.)	Nitrogen	8.0	14	23	30
	Nitrogen	6.2	17	27	36
	Nitrogen	5.4	18	32	41
	Air	6.2	16	28	36
110° (43° C.)	Nitrogen	8.0	38	56	67
	Nitrogen	6.2	40	70	>70
	Nitrogen	5.4	48	>70	>70
	Air	6.2	38	>70	....
100° (38° C.)	Nitrogen	8.0	100	170	210
	Nitrogen	6.2	120	230	310
	Nitrogen	5.4	170	300	400
	Air	6.2	130	210	280
75° (24° C.)	Nitrogen	8.0	>855	....	....
	Nitrogen	6.2	>855	....	....
	Nitrogen	5.4	>855	....	....
	Air	6.2	>855	....	....
Lot 2, initial sulfur dioxide content: 660 p.p.m.					
120° (49° C.)	Nitrogen	6.0	8	21	31
	Air	6.0	7	19	28
100° (38° C.)	Nitrogen	6.0	45	135	>185
	Air	6.0	42	125	>185
75° (24° C.)	Nitrogen	6.0	>625	....	....
	Air	6.0	>625	....	....

[b] Low, medium, high represent changes in optical density $\left(\Delta E^{2.5\%}_{1\text{ cm.},\ 420\ m\mu}\right)$ of 60, 180, and 300 x 10^{-3} units, respectively.

illustrative browning curves were drawn by inspection through experimental points. It may be noted that browning of the sulfited carrot goes through an "apparent induction period," followed by an essentially linear path. This situation usually prevails for the other sulfited vegetables studies, although deviation from linearity varies with initial sulfite content, kind of vegetable, and other factors. It is not possible, therefore, to express browning of these sulfited products as a straight-line

TABLE 4

Effects of moisture, atmosphere, and temperature on browning of dehydrated sulfited cabbage

Storage temp.	Atmosphere	Moisture (M.F.B.)	Days required for various degrees[1] of browning		
			Low	Medium	High
Lot 1, initial sulfur dioxide content: ca. 1000 p.p.m.					
°C.		%			
49	Nitrogen	7.1	0.7	1.4	2.0
	Nitrogen	3.5	1.8	4.0	5.8
	Nitrogen	2.1	6	13	18
	Air	3.5	2.0	4.4	6.5
43	Nitrogen	7.1	1.5	3.5	6
	Nitrogen	3.5	7	16	22
	Nitrogen	2.1	21	41	57
	Air	3.5	8	17	22
38	Nitrogen	7.1	3.5	8	12
	Nitrogen	3.5	18	42	63
	Nitrogen	2.1	64	140	>145
	Air	3.5	14	30	44
24	Nitrogen	7.1	60	160	240
	Nitrogen	3.5	330	>330	>330
	Nitrogen	2.4	>725	>725	>725
	Air	3.5	280	>725	>725
Lot 2, initial sulfur dioxide content: 930 p.p.m.					
49	Nitrogen	3.2	7	36	>80
	Air	3.2	6	31	>80
38	Nitrogen	3.2	24	74	120
	Air	3.2	21	64	104
24	Nitrogen	3.2	>670	....	....
	Air	3.2	>670	....	....

[1] Low, medium, and high represent changes in optical density $\left(\Delta E^{2.5\%}_{1\text{ cm., }420\text{ m}\mu}\right)$ of 40, 120, and 200 x 10^{-3} units, respectively.

function, as proved satisfactory for comparable samples of nonsulfited vegetables *(12)*.

RESULTS

Dehydrated White Potato

Effect of temperature. Temperature exerts a pronounced effect on rate of browning. For estimation of this effect, the logarithms of reciprocal days for a given degree of browning were plotted against the reciprocal of the absolute temperature as illustrated in Figure 2. (In the following discussions, the equivalent and more descriptive expression "average rate" will be used instead of "reciprocal time.") It is evident from the plot that the relation is approximately linear. The apparent activation energies range from 34 to 41 k.-cal., and the

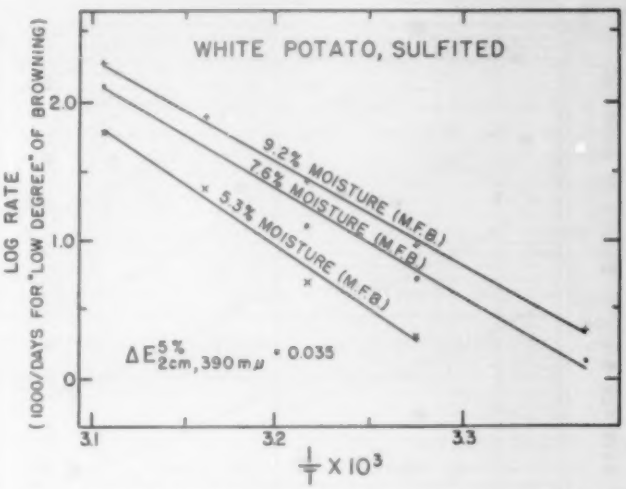

FIGURE 2. Effect of temperature on browning rate of sulfited white potato (Lot 1) at 3 moisture levels and packed in nitrogen.

Q_{10} values (change in rate per 18° F., or 10° C.) range from 5.7 to 7.7 (Table 5). These values increase progressively with decreasing moisture content. It may be noted that these are nearly the same for comparable samples of sulfited and nonsulfited products (Table 5).

Effect of moisture. It was found that average browning rate decreased markedly with lowering of moisture content. This is shown in Figure 3, where time for specified degrees of browning is plotted against moisture content. For purpose of alignment, the plotted values of time were taken from Arrhenius-type plots such as Figure 2.

It may be calculated from Figure 3 that the average rate of browning increases approximately 2-fold per 2% increase in moisture content. The effect becomes progressively greater with decreasing temperature.

The moisture effect was found reasonably constant for the various lots of dried sulfited potato investigated. A 2% increase in moisture content (from about 5.5 to 7.5 percent) resulted in 1.7, 1.8, 2.0, 2.4, 1.7, and 2.0-fold increases in average rate of browning at 120° F. (49° C.) for lots 1, 8, 9, 10, 11, and 12, respectively. In view of the similarity of moisture coefficients for products made from different lots of raw material, it

TABLE 5

Activation energies and Q_{10} values for browning process and sulfite loss in dried vegetables (sulfited and nonsulfited) packed in nitrogen

Commodity	Moisture (M.F.B.)	Activation energies, kcal.				Q_{10} values[1]			
		Browning			Sulfite loss	Browning			Sulfite loss
		Nonsulfited	Sulfited			Nonsulfited	Sulfited		
			Low[j]	High[k]			Low[j]	High[k]	
	%								
White potato, Lot 1	9.2	36	34	34	33	6.2	5.7	5.7	5.3
	7.6	38	36	36	35	6.9	6.2	6.2	5.9
	5.3	40	41	....	40	7.6	7.7	....	7.5
Carrot, Lot 1	8.0	38	35	35	36	6.7	5.9	5.9	6.2
	6.2	39	36	39	39	7.0	6.3	7.0	7.2
	5.4	39	40	41	41	7.3	7.6	8.0	8.0
Cabbage, Lot 1	7.1	....	35	35	....	....	5.8	5.8	....
	3.5	....	38	42	....	....	6.8	8.7	....
	2.1	....	42	42	....	....	8.3	8.4	....

[j, k] Calculated for low and high degrees of browning. See footnotes to Tables 2, 3, and 4.
[1] Temperature range, 39° to 49° C.

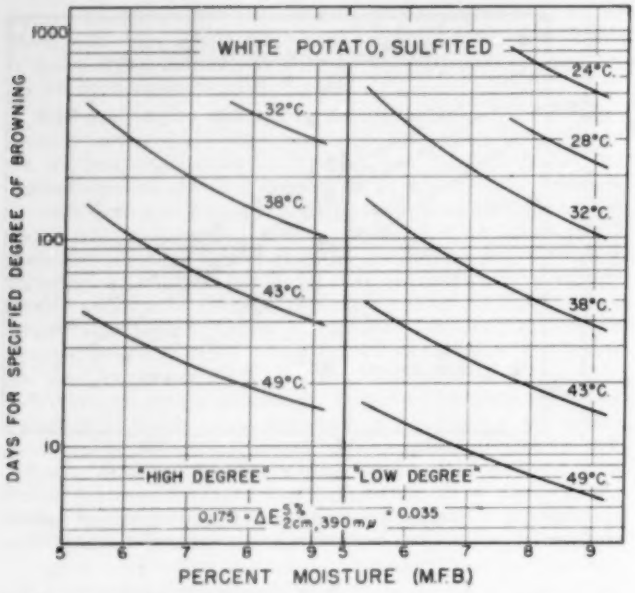

FIGURE 3. Effect of moisture content and temperature on browning of dried sulfited (ca. 340 p.p.m.) white potato (Lot 1) packed in nitrogen.

appears that the moisture vs. browning, Figure 3, may be used for estimation of moisture effects for other lots of dried sulfited white potato.

It is interesting that the moisture coefficients found for dried sulfited potato are about the same as those readily calculated for nonsulfited white potato from previously reported data *(12)*. Thus, the coefficients at 120° F. (49° C.) calculated for five different lots (not related from standpoint of raw material to the sulfited samples listed above) of nonsulfited white potato are as follows: 1.6, 1.9, 1.9, 2.0, and 2.0. Similar values have been reported by Ross *(19)*.

Effect of oxygen. Package atmosphere (air vs. nitrogen) has little apparent effect on the average rate of browning. From data in Tables 2 and 6, it is calculated that average rates in air usually fall within a range of 0.8 to 1.2 times the corresponding rates in nitrogen. Evaluation of the effect of oxygen is complicated to the extent of any bleaching of water soluble natural pigment which may occur and thus interfere with measurement of color change during storage. Such bleaching has been observed in dehydrated white potato at —30° F. (—34° C.), but not in samples stored at 75° F. (24° C.) and higher.

Dehydrated Carrot

Effect of temperature. The temperature coefficients found for browning of dried carrot are similar to those observed for dried white potato. The Q_{10} values range from 5.9 to 8.0 for products ranging in moisture content from 8.0 to 5.4%, respectively. These Q_{10} values correspond to apparent activation energies of 35 to 41 kcal. (Table 5). As in the case of dried potato, there is fairly good agreement between Q_{10} values for browning of comparable samples of sulfited and nonsulfited carrot (Table 5).

Effect of moisture. For dried carrot the average browning rate was affected less by lowering the moisture content than was found to be true for white potato.

TABLE 6

Sulfited white potato. Comparison of observed days for "high degree" [m] of browning with values estimated from alignment chart (Figure 3)

Lot	Storage temp.	Atmosphere	Moisture (M.F.B.)	Sulfite content, p.p.m. SO_2	Days required for "high degree" [m] of browning	
					Observed	Estimated
	° C.		%			
2	49	Nitrogen	8.0	400	21	19
	49	Air	8.0	400	21	....
	38	Nitrogen	8.0	400	177	150
	38	Air	8.0	400	155	....
8	49	Nitrogen	5.0	220	57	44
	49	Air	5.0	220	52	....
	49	Nitrogen	8.6	220	20	17
	49	Air	8.6	220	16	....
	38	Nitrogen	8.6	220	120	120
	38	Air	8.6	220	92	....
9	49	Nitrogen	4.8	600	55	46
	49	Air	4.8	600	45	....
	49	Nitrogen	7.0	600	25	24
	49	Air	7.0	600	22	....
	38	Nitrogen	7.0	600	170	200
	38	Air	7.0	600	130	....
10	49	Nitrogen	5.1	500	85	42
	49	Air	5.1	500	82	....
	49	Nitrogen	7.5	500	28	22
	49	Air	7.5	500	22	....
	38	Nitrogen	7.5	500	190	160
	38	Air	7.5	500	140	....
11	49	Nitrogen	5.1	260	35	42
	49	Air	5.1	260	30	....
	49	Nitrogen	8.8	260	14	16
	49	Air	8.8	260	10	....
	38	Nitrogen	8.8	260	91	110
	38	Air	8.8	260	75	....
12	49	Nitrogen	5.0	670	59	44
	49	Air	5.0	670	50	....
	49	Nitrogen	7.7	670	22	21
	49	Air	7.7	670	19	....
	38	Nitrogen	7.7	670	120	150
	38	Air	7.7	670	110	....

[m] $\Delta E \frac{5\%}{2\text{ cm.}, 390\text{ m}\mu}$ equals 0.175 units of optical density.

Thus, it may be calculated from data of Table 3 that a 2% increase in moisture content resulted in a 1.2- to 1.6-fold increase in average browning rate at 120° and 100° F. (49° and 38° C.), respectively.

Effect of oxygen. As in the case of dried potato, package atmosphere has little apparent effect on the average rate of browning. From data of Table 3, it is

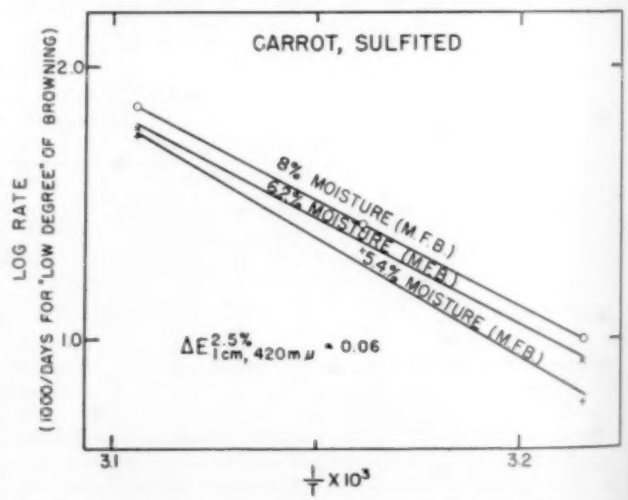

FIGURE 4. Effect of temperature on browning rate of sulfited carrot (Lot 1) at 3 moisture levels and packed in nitrogen.

calculated that average rates in air fell within a range of 0.9 to 1.1 times the corresponding rates in nitrogen. Of course, these measurements are subject to the same possibility of error from bleaching as was mentioned for white potato.

Dehydrated Cabbage

Effect of temperature. The temperature coefficient for browning of cabbage is also high. The Q_{10} values range from 5.8 to 8.7 for samples ranging in moisture content from 7.1 to 2.1%, respectively. These values correspond to activation energies of 35 to 43 kcal. (Table 5).

Effect of moisture. The average browning rate of dried sulfited cabbage is decreased greatly by lowering moisture content. It is evident in Figure 6 that this effect becomes more pronounced as the product approaches complete dryness. For example, at 120° F. (49° C.) increase of moisture content from 5.1 to 7.1% resulted in 1.7-fold increase in browning rate, whereas a change of moisture content from 2.1 to 4.1% led to a 4.6-fold increase in rate of browning.

Effect of oxygen. From data of Table 4, it is calculated that average rates of browning of cabbage (Lot 1) in air fell within a range 0.9 to 1.4 times the corresponding rates in nitrogen. A similar comparison of data for Lot 2 dried cabbage shows a range of 1.1 to 1.2. Thus, it appears that the oxygen effect, if any, must be relatively small.

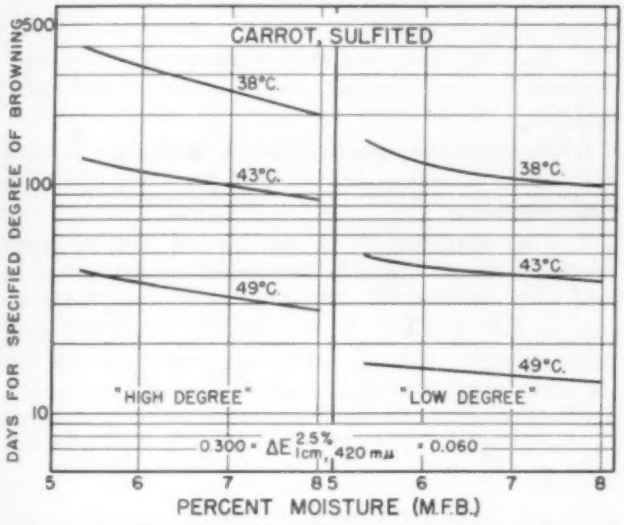

FIGURE 5. Effect of moisture content and temperature on browning of dried sulfited (ca. 1900 p.p.m.) carrot (Lot 1) packed in nitrogen.

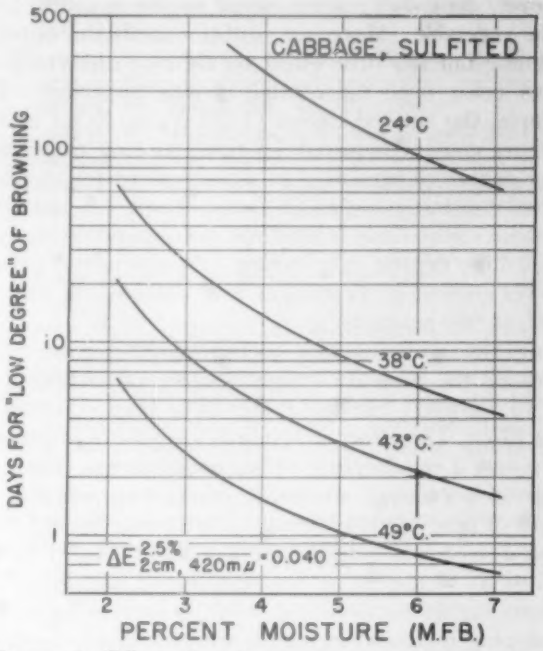

FIGURE 6. Effect of moisture content and temperature on browning of dried sulfited (ca. 1000 p.p.m.) cabbage (Lot 1) packed in nitrogen.

DISCUSSION

Effect of sulfite. It is generally recognized that sulfite retards browning of dehydrated vegetables; however, the magnitude of the effect is largely unknown. For the purpose of throwing some light on this question, comparative data on browning of sulfited and nonsulfited vegetables have been assembled in Table 7. The values for sulfited products are from Figures 3 and 5, while those on nonsulfited vegetables are from the previous report *(12)*.

It is evident in Table 7 that sulfite, in the concentrations used, greatly retards the browning of dehydrated carrot and white potato. The degree of retardation,

TABLE 7

Effect of sulfite on browning of dried vegetables. Time required for equal degrees of browning in comparable samples of sulfited (S) and nonsulfited (NS) products stored at 38° C. (100° F.)

Commodity	Moisture (M.F.B.)	Package atmosphere	Days required for various degrees[a] of browning								
			Low			Medium			High		
			S	NS	S/NS	S	NS	S/NS	S	NS	S/NS
	%										
Carrot, Lot 1[b]	8.0	Nitrogen	100	22	4.5	160	66	2.4	200	110	1.8
	6.2	Nitrogen	120	34	3.6	220	100	2.2	310	170	1.8
	5.4	Nitrogen	160	44	3.6	300	130	2.3	400	220	1.8
	6.2	Air	130	36	3.6	210	108	1.9	280	180	1.6
Carrot, Lot 2	6.0	Nitrogen	45	24	1.9	135	72	1.9	.....	.....	.....
	6.0	Air	42	25	1.7	125	75	1.7	.....	.....	.....
White potato, Lot 1[b]	9.2	Nitrogen	36	8	4.5	76	24	3.2	103	40	2.6
	7.6	Nitrogen	57	17	3.4	110	51	2.2	160	84	1.9
	5.3	Nitrogen	160	47	3.4	320	140	2.3	460	240	1.6
	7.6	Air	66	13	5.1	125	39	3.2	162	66	2.5

[a] Low, medium, high—See footnotes to Tables 2 and 3.
[b] Data for sulfited samples from Figures 3 and 5; data for nonsulfited from previous report *(12)*.

however, depends to some extent on the moisture level of the vegetable. Moreover, sulfite retards the onset of browning but has little effect on the rate of increase in brown color once the change is well underway. For example, the sulfited carrot (1920 p.p.m. SO_2) at .8% moisture content required 4.5 times as long to produce a low degree of browning as was required for the non-sulfited control; whereas the factor is only 1.8-fold when the same comparison is made on corresponding samples with a high degree of browning. As one would expect, a lower degree of protection was obtained in carrots, Lot 2, at 660 p.p.m. SO_2.

For the white potato, sulfite (330 p.p.m. SO_2) increased the time for "high" degree of browning by 1.9- to 2.6-fold. Similar values have been reported by Ross *(19)*. The effect of sulfite is even more impressive when only a small degree of browning occurs. Over the range of conditions studied in these experiments, the length of time for low degree of browning ranged from about 2- to 5-fold longer (average about 4-fold) for the sulfited as compared to the nonsulfited samples. This appears highly significant in view of current interest in developing methods for maintenance of dried vegetables without appreciable change during storage.

Effects of temperature and moisture. Lowering of moisture content offers great advantage in stabilization of dried vegetables against browning at elevated temperatures. It is recognized that this point was considered in establishing specification moisture levels for dried vegetables procured during World War II. Figures 3, 5, and 6 show the advantages that can be realized from further reductions in specification moisture. [For white potato, 7% moisture by the 6-hour method *(20)* is equivalent to about 9% as determined by the procedure of Makower, et al. *(14)*; for carrot the corresponding figures are 4% and about 6.5%. For cabbage the two methods yield similar values.] According to Figure 3, lowering of specification moisture level of sulfited white potato approximately 4% would result in products that would suffer only a low degree of browning in the course of 6 months of storage at 100° F. (38° C.). In case of cabbage (Figure 6) it is evident that moisture content would have to be reduced to a very low level in order to achieve a similar degree of stability.

As the relation shown in Figure 3 is derived from a single lot of white potato, it is of interest to note how "storage life" (time for a specified degree of browning) predicted by the chart compares with observed values for other lots of dried potato (Table 6). Agreement between observed and estimated values is quite satisfactory, despite variations in sulfite and sugar contents (Table 1) between the samples under comparison. As more information is obtained on the quantitative effects of these two variables, it should be possible to make predictions of "storage life" based on compositional data with more certainty.

Accelerated storage tests. It has long been recognized that an accelerated storage test is needed for evaluation of the adaptability of raw materials for manufacture of dehydrated vegetables suitable for military use. The high temperature and moisture coefficients suggest the possibility of devising a test of this kind. From the magnitude of the coefficients it appears reasonable that a 2-day test would be feasible.

CONCLUSIONS

1. The browning of dried sulfited carrot, cabbage, and white potato usually proceeds through an apparent induction period followed by an approximately linear path. This is in contrast to the behavior of dried non-sulfited vegetables, in which browning usually proceeds in approximately linear fashion.

2. It was found that inhibition of browning by sulfite depends in part on the moisture level of the vegetable.

3. Average rates of browning of dried sulfited carrot, cabbage, and white potato were found to vary in approximately exponential fashion with the reciprocal of absolute temperature. It was found that the average rates of browning of the three vegetables increased approximately 6- to 8-fold per 18° F. (10° C.) rise in temperature. The effect of temperature becomes progressively greater with decreasing moisture content.

4. Rate of browning of the dried vegetables decreased markedly upon lowering of moisture content. Decrease in average rate per 2% decrease in moisture content varied from 1.2- to 4.6-fold, depending on kind of vegetable and moisture level. Browning rate was more affected by reduction of moisture in dried cabbage and white potato than in dried carrot. The moisture effect increased as the product approached complete dryness.

5. There is close similarity between effects of temperature and moisture on rates of browning and sulfite loss.

6. Package atmosphere (air vs. nitrogen) showed little effect on rate of browning of the three dried sulfited vegetables.

7. The combination of sulfite and low moisture greatly prolongs the time that dried vegetables can be held without detectable change at an elevated temperature, as 100° F. (38° C.), for instance. For dried white potato, time for a barely visible degree of browning was increased about 16-fold through use of 330 p.p.m. SO_2 and reduction of moisture content from 9% (equivalent to the "7%" Q.M.C. specification *(20)* moisture content) to 5%.

Acknowledgments

The authors wish to acknowledge the guidance of L. B. Howard and J. R. Matchett and the helpful suggestions of A. N. Prater and B. Makower. Appreciation is expressed also for the cooperation of L. R. Leinbach, Doris H. Taylor, N. Floy Bracelin, and D. C. Patterson.

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Incidence and Significance of Microorganisms in Citrus Juices[a,b,c]

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(Manuscript received May 5, 1951)

Microbiological examinations of 157 batches of citrus juice, including 112 orange, 30 grapefruit, and 15 tangerine, indicate that juices extracted under the most ideal conditions may contain a wide range of microorganisms. Evidence is presented to show that the citric acid content of the fruit used is one of the most important factors involved. The significance of the presence of microorganisms in citrus juices is discussed.

External surfaces of citrus fruits, like other fruits and vegetables, harbor many different types of microorganisms. The high moisture, sugar, and organic acid contents of citrus juices particularly favor the growth of yeasts. It is essential that the juice be maintained as free as possible from microorganisms during its extraction and subsequent processing, particularly if the juice is to be used for the production of a frozen concentrate. For one reason, the fewer the number of microorganisms in a frozen concentrate, the better will be its chance of resisting spoilage due to improper handling between the time it is produced and the time the consumer uses it; furthermore, a low-count juice is considered to be evidence of a sanitary plant. Despite all precautions, however, microorganisms do get into the juice and sometimes in relatively large numbers.

It would appear, therefore, that a knowledge of the source of these organisms would be necessary before any significance could be attached to their presence in the finished product. The most logical sources of contamination would appear to be (a) the external surfaces of the fruit, (b) the equipment used and (c) the interior of the fruit. If these organisms are entering the juice from the outside of the fruit, the possibility that they might have a sanitary significance would be greater since citrus fruits are subject to contamination by handling and occasionally by spray irrigation of the trees with lake water. If, on the other hand, the plant equipment should be the primary source of infection, then the problem would be primarily one of plant sanitation and should be controlled by rigid sanitary inspection. The investigations reported in this paper show that the most likely source of microorganisms in the juice is the interior of the fruit itself and therefore will undoubtedly be the most difficult to control.

IMPORTANCE OF SURFACE MICROORGANISMS

A study of the ratio of surface area of the average citrus fruit to the volume of juice extracted from the fruit suggests that it is highly improbable that those organisms remaining on the fruit after washing could

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[b] Cooperative research by the Florida Citrus Experiment Station and the Florida Citrus Commission, Lake Alfred, Florida.
[c] Florida Agricultural Experiment Station Journal Series No. 1.
[d] Florida Citrus Experiment Station, Lake Alfred, Florida.
[e] Florida Citrus Commission, Lake Alfred, Florida.

contribute much to the total count in the extracted juices, even if all entered the juice during the extraction process. This assumption is justified by the experiences of the authors who have been unable to correlate surface counts of oranges with the counts obtained from the extracted juices. Similarly, the spraying of fruit with indicator organisms such as *Serratia marcescens* and *Escherichia coli* and attempts to recover these subsequently from the extracted juices have been unsuccessful, even when the sprayed fruit was extracted without a preliminary washing.

These views are in agreement with those of Patrick *(2)*, who made a thorough bacteriological study of Florida citrus processing plants and concluded that although fruit quality was of major importance, the use of fruit with clean exteriors did not insure a low count juice from the extractors.

It is probable that many of the bacteria which resist the rinsing action of rains, the toxic action of sunlight, and certain of the various sprays used on citrus trees die rapidly once they are in contact with the high degree of acidity in citrus juices.

IMPORTANCE OF CLEAN EQUIPMENT

The maintenance of a sanitary plant is undoubtedly as important in the citrus processing industry as it is in any other food industry. Although the acidic nature of the juice, the type of equipment used, and the nature of the process itself tend to minimize the build-up of microorganisms, there is the possibility that organisms will multiply in the equipment, particularly in the evaporators used in the production of frozen concentrate, if too long a period is allowed to elapse between major clean-ups.

The ideal equipment, of course, would be of such design that all surfaces with which the juice could come in contact would be continuously flushed with the flowing juice. Such equipment would practically preclude any possibility of build-up since the production of frozen citrus juice concentrates is usually a continuous process and of sufficiently short duration that multiplication of microorganisms in the juices between the time of extraction and freezing would be negligible.

In view of the excellent sanitary practices recommended to and employed by most of the concentrate plants, it is doubtful that the equipment in the average plant contributes much to the total count in the juices. Nolte and von Loesecke *(1)* indicated that such might be the case when they found a wide range of counts in juices obtained from various canning plants and could not establish a correlation between the variation in counts and the apparent cleanliness of the plants.

IMPORTANCE OF FRUIT QUALITY

The quality of the fruit used in the production of frozen concentrated citrus juices is probably the most important single factor to be considered in the maintenance of a consistently low count product. The consequence of using unsound fruit has been clearly demonstrated by Wolford and Berry *(3)*. Juice prepared from "soft rot" oranges was found to contain 2500 times as many organisms as juice prepared in the same manner from sound fruit. The count of approximately 13 million organisms per ml. which these workers obtained from the juice of "soft rot" fruit is an extreme case although rather wide variations in counts can be obtained from apparently sound fruit.

Table 1 illustrates the wide range of counts which might be expected when citrus juices are extracted from carefully graded fruit on a semi-commercial scale and when all conditions are maintained as ideal as possible. Each sample represents an average of approximately 200 gallons of freshly extracted juice and all samples were plated immediately after collection on Difco dextrose agar (pH 7.0) for an approximate total count and on acidified Difco potato dextrose agar (pH 3.5) for a yeast and mold count.

The 157 separate runs included in Table 1 were made over a period of two canning seasons and included the usual canning varieties: Hamlin, Pineapple, and Valencia oranges, Duncan and Marsh grapefruit, and Dancy tangerines. The fruit used in these runs were tree-picked, carefully graded, efficiently washed, and juiced in the experimental pilot plant located at the University of Florida Citrus Experiment Station. In order to minimize the possibility of contamination from equipment, the rotary juice extractors, holding tanks, and lines were washed with a hot detergent before each run and all exposed surfaces were thoroughly steamed.

Despite these precautions there was a wide variation of counts from the extracted juices. For example, the range in the case of oranges extended from a minimum count of 1,200 organisms per ml. to a maximum of 745,000, with an average count of 59,000 organisms per ml. for the 112 separate runs. It is interesting to note that grapefruit, having generally the highest citric acid content, had an average yeast and mold count which was approximately one-third of the total count, while in the tangerine juices of relatively low acid contents the yeast and mold count was less than 2% of the total count.

The relationship between the citric acid content of the fruit and the number of microorganisms in the extracted juices is shown by the histogram in Figure 1, in which the average counts of juices between definite citric acid levels is plotted against the acid range. Counts obtained from orange juice with citric acid con-

TABLE 1

Variability of numbers of microorganisms in freshly extracted citrus juices

Kind of fruit	Number of samples	Total microorganisms/ml.			Yeasts and molds/ml.		
		High	Average	Low	High	Average	Low
Orange	112	745,000	59,000	1,200	217,000	15,000	600
Grapefruit	30	148,000	36,000	1,200	68,000	13,000	200
Tangerine	15	13,000,000	2,400,000	20,000	134,000	44,000	7,300

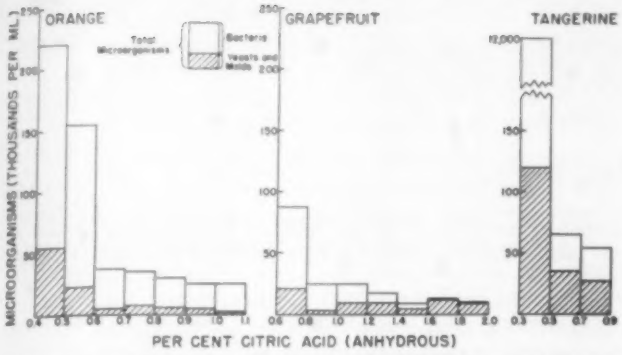

FIGURE 1. Relationship between citric acid content and microorganisms in citrus juices. (Averages of the total counts of juices between definite acid limits plotted against the acid range.)

tents above 0.6% were generally low, less than 50,000 organisms per ml., while low-acid juices had much higher average counts. Similar trends are apparent in the case of grapefruit and tangerine juices. Above 1.6% citric acid the yeast and mold count in grapefruit juice was essentially the same as the total count, while yeasts and molds contributed but little to the total counts of tangerine juices containing less than 0.5% acid.

The scatter diagram in Figure 2 shows the distribution of total counts in 80 samples of orange juice with reference to the acid content of the juice. It is significant that none of the 54 samples containing 0.7% or more of citric acid had a total count greater than 100,000 microorganisms per ml., while one-half of the 26 samples containing a lesser amount of acid had a total count of 100,000 or more organisms per ml. Since this figure has been set as an arbitrary standard by some of the larger processors of frozen orange concentrate, the effect of fruit maturity should be considered.

In view of the fact that an insufficient amount of time elapsed between the extraction of the juice and the plating of the samples to permit multiplication of the acid-tolerant organisms, it seems logical to assume that the organisms were already present in the fruit at the time of extraction. Work now in progress indicates that in addition to yeasts, there are several species of bacteria which are able to grow in orange juice at a pH of 4.0 or even lower in certain instances. It also appears that these bacteria, when inoculated into mature oranges on the tree, are able to multiply either with or without visible evidence of deterioration of the fruit.

SUMMARY

One of the most important factors in the production of a low-count concentrate is the maturity of the fruit. In spite of the usual precautions, such as plant sanitation and efficient washing and grading of fruit, the use of over-mature, low-acid fruit will often result in a high-count product. It is believed that this factor should be taken into consideration in any attempt to standardize citrus juices on the basis of microbiological examinations.

Although the majority of bacteria will die rapidly in such an acid environment as is found in citrus juices, a few bacteria and many yeasts are able to multiply either in the extracted juice or even in the fruit when provided a method of entry.

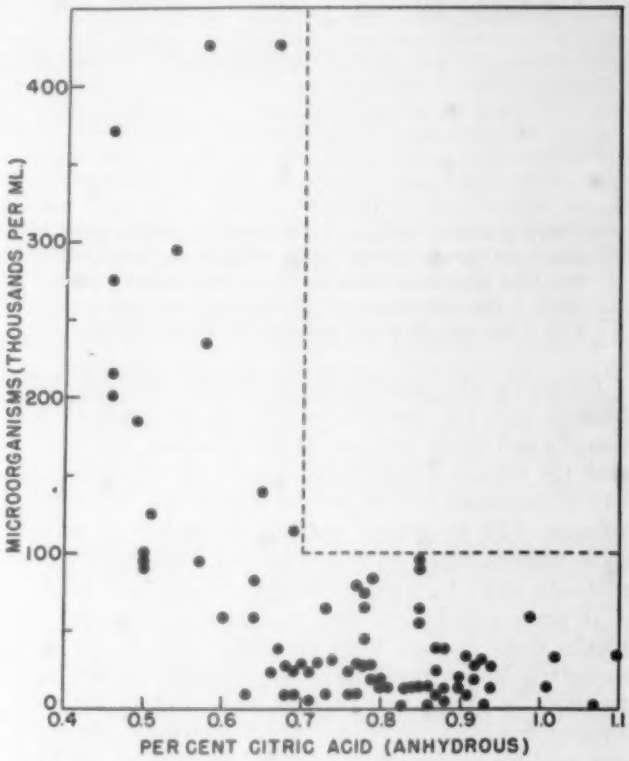

FIGURE 2. Effect of citric acid content on the distribution of total counts of 80 samples of orange juice.

Acknowledgment

The authors are indebted to Mr. Richard Huggart and Miss Dorothy M. Asbell of the Florida Citrus Commission for the chemical analyses cited in this paper.

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A Program for Increased Returns from By-product Operations

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(Manuscript received May 28, 1951)

New processes adopted for recovery of salable products from meat packing plant effluent are described. By these processes losses of grease are reduced from 12 to 3 lbs. and losses of nitrogen are reduced from 3 to 2 lbs. per thousand pounds live weight killed.

Following the conclusion of World War II, John Morrell and Co. launched a special program on by-product and waste recovery at its Ottumwa, Iowa, plant with the following broad objectives as the ultimate goal: (1) a decreased loss of protein and grease in its plant effluent, (2) improved nutritional quality of animal feeds manufactured by improvements in equipment and methods, and (3), a more efficient utilization of labor.

In years gone by and even in a number of present day plants, meat packers were generally blind to the large monetary losses resulting from valuable by-products, particularly grease and protein, being lost in the plant effluent and from the breakdown of proteins in the edible and inedible rendering and drying operations. In 1945, the Ottumwa plant of John Morrell and Co. was discharging sewage to a public waterway which would average about 3 lbs. of nitrogen per thousand pounds of live weight killed and more than 12 lbs. of grease per thousand pounds live weight killed. Through exhaustive laboratory tests and much field work it was estimated that these figures could be reduced to approximately 1.5 lbs. of nitrogen and 2.0 lbs. of grease per thousand pounds live weight killed.

The first project on the program was to separate grease bearing waste waters from non-grease bearing and to build two large automatically skimmed primary settling basins completely equipped with grease and sludge sweeps and sludge pumping equipment. One basin was provided to handle the grease-bearing waters from the pork operations and a second basin to handle waste from the beef and sheep operations. By such an arrangement the skimmings from the beef and sheep basins could be rendered as inedible tallow and normally sold at a higher price than if the pork, beef and sheep wastes were combined in a single settling basin and the resultant skimmings rendered out as brown or high acid yellow grease.

The pork basin was designed to be 112 ft. 2 in. long, 8 ft. wide, and varying in depth from 5 ft. 9 in. at the effluent end to 7 feet deep at the influent end. It was designed to handle flows up to a rate of 2 million gallons per day. The beef basin was to be 74 ft. long, 7 ft. wide, and 4 ft. 6 in. to 5 ft. 6 in. deep and handle flows up to a rate of 0.5 million gallons per day. Both of these basins were equipped with vertical concrete baffles at their influent ends to break up the initial entrance velocity of the influent waters. In addition, a sludge hopper was provided at the influent end of each basin. Also, two pumps of 300 gallons per minute capacity pumping against a 22 foot head were provided for sludge removal from each basin. The basins were placed in service in 1948, and effected a reduction of grease in the plant effluent to about 5 lbs. per thousand pounds live weight killed.

Following the installation of the settling basins, consideration was next given to the problem of high residual grease content in the 50% protein meat and bone scraps obtained from dry rendering inedible pork and beef products. Grease values of 10 to 12% were consistently obtained in manufacturing this feed supplement. However, that grease provided no monetary return to the company, inasmuch as all of the meat and bone scraps were sold on a guaranteed 50% protein basis. After considerable investigation of various processes available to reduce this residual grease, the decision was reached to install a solvent extraction plant using trichlorethylene as the solvent.

A batch type extraction plant, whose principal units include a jacketed extractor, an extractor condenser, a miscella still and condenser, a vapor recovery system, and numerous pumps and storage tanks, was selected as best suited to our needs. The John J. Dupps Company of Cincinnati, Ohio, designed and built the plant with considerable technical aid being given by engineers from E. I. DuPont de Nemours on the construction and operation of this plant.

Although estimated operating costs were higher using trichlorethylene compared to some other solvents, the non-explosive characteristics of the solvent dictated its selection since the extraction plant had to be installed in close proximity to other buildings.

The unit selected had a capacity of 4,000 lbs. of cracklings per charge and was capable of handling between 4 and 5 charges per 24 hour day. If no expelling were employed, the grease content of the initial charge would be approximately 35% and would reduce to approximately 4.5% using three solvent washes. Normal continuous screw pressing operations give a press cake that analyzes between 10 and 12% grease. Thus, 4 to 6 lbs. of grease for each 100 lbs. of cracklings charged would be gained by using solvent extraction.

Comparisons between the cost of solvent-extracting grease from inedible cracklings and mechanically pressing grease from cracklings show that if the extraction system is operated on a 24 hour day basis, the added return exceeds $100.00 each day. Of course, the fixed costs on equipment, labor, and the utilities required are greater on the extraction process but the gain of the additional grease at present day prices more than offsets these higher costs. If the tonnage of cracklings to be extracted was much larger, additional returns could be gained by converting the batch unit to a continuous extraction system, thereby reducing utility costs, solvent losses, and labor costs.

The low-fat 50% protein meat and bone scraps feed supplement from solvent extraction is thought to have a higher nutritive value than the high-fat supplement previously produced.

Numerous operating difficulties have been encountered in operating the extraction plant, but these prob-

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lems are recognized and are being dealt with to further improve its operating efficiency. Some of the troubles encountered were the large quantity of fines tending to plug the filter pockets on the extractor, or if passed by the filter pockets, causing stoppages in the still. The solvent vapor recovery system presented numerous problems before good operation was attained. An absorption oil which would not become gummy or carbonize at high temperatures has been difficult to find.

Perhaps the most progressive step taken in the program to get a larger return from by-products operations was the adoption of a new continuous centrifugal method for separating solids and grease from tank water produced in both the edible and inedible wet rendering operations. The generally accepted practice of present day wet renderers consists of blowing the residue from the wet rendering tanks into a holding vat or "slush box." This residue or "slurry" is subjected to heat and allowed to stand for a minimum of 24 hours. The grease, which comes to the surface in this settling out period, is then skimmed off and mixed with other rendered inedible greases. A portion of the supernatent liquid is decanted and the low-grease slurry remaining after skimming and decanting is then dropped onto cloths, retained on plattens, and placed in a large vertical or horizontal press. Pressure is applied to extrude as much water as possible from the cake, the water so removed being collected for later concentration by evaporation into stick liquor. The press cake is removed from the cloths on the plattens and subsequently mixed with dried blood and stick and charged into rotary dryers to produce 60% protein meat meal. Disadvantages of this system are the high labor costs, large space requirements for slush boxes to permit holding the rendering tank residue for 24 hours or longer, the large monetary loss due to protein degrading to ammonia during the holding period, and the poor sanitary conditions which go hand in hand with this method of handling wet tankage.

Working with the Sharples Corporation, a system was developed whereby the solids, grease, and water by-products resulting from the wet rendering operations, the slime strippings from the casing cleaning operations, and numerous other solids bearing protein water could be handled with dispatch through a size-reducing hammer mill, a controlled temperature mixing tank, and a Sharples P-14 Super-D-Canter to effect the separation of the solid material from the grease-bearing, high-protein water. In this sequence of operations, the grease particles intermixed with the solids are washed away from those solids in the slurry tank by high-speed agitation and are carried away with the protein water.

The solids discharged from the Sharples P-14 Super-D-Canter have a moisture content of approximately 50%, are low in grease, analyzing less than 6% grease on a dry basis compared with 10 to 12% in solids from presses, and are of a fluffy characteristic especially suited for later drying. It is quite probable that the tankage produced from this material has superior nutritive qualities due to the rapidity with which it is handled and the low grease content in the end product.

The high-protein tankwater discharged from the Super-D-Canter is pumped over a 40-60 mesh stainless steel shaker screen to remove the larger suspended solids. The screened liquid, containing grease, water and soluble and insoluble solids, is then heated to slightly above 200° F. (93° C.) and passed through a Sharples H-2 nozljector to effect a continuous separation of the grease from the tankwater. The nozljector centrifuge has a series of tangentially located nozzles around the edge of the bowl which makes it possible to continuously handle two phase separation of liquids containing fine solids. The degreased tankwater, having a grease content of less than one-half of 1%, is then sent to Swenson quadruple effect, low temperature, low pressure evaporators, or is sent to storage towers for mixing with other high-protein waters and then pumped to the Swenson evaporator feed tank. The tankwater is evaporated to a 30° Bé, molasses-like substance with a protein content of 50 to 60%. This substance is then mixed with coagulated blood and the wet tankage delivered by the Super-D-Canter and charged into a rotary type dryer. This mixture is dried until the moisture content is less than 7% and the protein in the mixture ready for sacking is not less than 60% (determined as N × 6.25).

Only twenty minutes are required to complete the separation of solids, grease, and tankwater from the time the rendering tank solids leave the slush box, using the continuous centrifugal process. Using the hydraulic press method, the slurry is held in the slush box for at least 24 hours before any pressing is done. This long holding results in a large percentage of protein breakdown.

We have adopted the practice of separating grease-bearing waters from non-grease bearing waters which are rich enough in protein to warrant evaporation, and subsequently degreasing these grease-bearing waters by centrifuging prior to evaporation. By so doing, the heat transfer performance of the Swenson evaporators has been maintained at a high level and the down time for cleaning has been held to a minimum. Also, by preventing a dilution of greasy waters by grease free waters, a greater recovery of grease has been attained.

The advantages thus gained by adoption of the Sharples process equalled or exceeded expectations in that: (1) The process effects maximum recovery of by-products and is continuous; (2) the system can be operated by one employee; (3) a maximum separation of grease from the solids and tankwater is obtained; (4) loss of protein is decreased tremendously, and the odors formerly accompanying the process are eliminated; (5) it eliminates loss of product through spillage with resultant decrease in clean-up costs; and (6) it reduces biochemical oxygen demand in the plant's effluent.

Upon completion of these three projects, the results obtained were still not all that could be desired. Additional investigational work was given to the primary settling basins, and from these studies it was found that influent waters were short circuiting directly to the discharge weir along the floor of the basin. Studies indicated the cause to be the concrete influent baffle. This baffle was removed and in its place a fan-shaped discharge weir was installed in such a manner that the influent was delivered at the basin's water level and was equally distributed across the width of the basin. A multi-paddle grease wiper was also designed to replace a single-bladed wiper to improve the automatic skimming operations. By these changes, the retention time in the basin was increased approximately 50%; the grease skimmed from the basin was more free of adhering, non-grease solids; the weight of the settleable solids was materially increased; and evidences of septic action at the effluent end of the basin were eliminated. Automatic time-cycle controllers have been installed to operate the grease sweep, grease wipers, and sludge pumps to further aid in the recovery of by-products with a minimum expenditure of labor.

Because of the aforementioned changes in our processing methods, the plant effluent now averages approximately 2 lbs. of nitrogen and 2 to 4 lbs. of grease per thousand pounds live weight killed. Study and research are still being devoted to these before mentioned processes and a number of other by-product operations wherein there are possibilities that income can be derived from products now being lost in the plant effluent. Continued research is required because of the high degree of competition in the meat packing industry. It behooves each packer to prevent the loss of every pound of by-product that is humanly possible, since it is this end of the business that will determine the profit or loss at the end of the year's operation.

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Binomial Systems and Organoleptic Analysis[a]

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Several simple test systems have been used to measure differences in the sensory characteristics of food products. When only two samples, A-B, are presented to a judge, the test is called a paired difference, a quality judgment, a preference, or a consumer acceptance test. When three samples, AA-B, are employed, the test is called a triangle difference test.

The basic statistical principles underlying these tests are discussed in order to focus attention on their binomial similarity and to correlate the tests with more complex systems. These latter include symmetrical systems such as AA-BB and AAA-BBB and asymmetrical systems such as AAA-B, AAAA-B, and AAA-BB. The chance probability, usefulness, and limitations associated with each of the systems are presented.

The properties of a true difference test, a quality judgment test, and the preference tests are reassessed and clarified. Both one-judge and more-than-one-judge panels are discussed in connection with the various binomial systems.

Industrial and research laboratories often find themselves faced with the necessity of acquiring information about the organoleptic properties of foods and food products. They have become increasingly aware of the importance of experimental design and statistical analysis as fundamental and potent tools with which to attack organoleptic problems sensibly and scientifically. Experimental designs based on two-sample and three-sample systems are familiar to professional personnel in the food industry. The two-sample test has been called a consumer acceptance test, a preference test, a quality judgment test, or a difference test. The three-sample test is generally known as a triangle difference test. Although these tests have been used practically, discussed and modified in an attempt to gain greater control over environmental, inheritable, and psychological factors, it is still possible to add a few words about some of their basic characteristics and to mention other tests, members of the same family, each of which have some specific utility in food laboratories.

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BINOMIAL TEST SYSTEMS

As the mathematical concept underlying all these tests, their modifications and extensions, is the binomial theorem, it is proposed that they be called generically "binomial tests." Such nomenclature would focus attention upon their basic similarity and divert attention from the minor differences that heretofore have played a major role.

Familiar binomial tests, the two-sample and the three-sample systems, have been mentioned briefly and for purposes of comparison may be called A-B and AA-B systems. Other types of binomial systems have been proposed for use in organoleptic research on food products, but a search of the literature has not revealed any instance of their having been used for this purpose. Wood *(9)* discussed theoretical systems made up of two sets of samples, both of which contain an equal number of subsamples, for example, AA-BB, AAA-BBB, and so forth to AAAAAA-BBBBBB. The chance probabilities for each system are given. Wood's discussion was based on Fisher's tea test *(2)*, also a theoretical system designed to measure sensory discrimination. The tea test design has been used to advantage by Harris and Kalmus *(4, 5)* who studied taste sensitivity toward phenylthiourea and related compounds.

All the binomial modifications mentioned, with the exception of the triangle (AA-B) test, consist of equal numbers of representative portions of two different items such as (A-B and AA-BB) and may be called symmetrical binomials. The triangle test is an asymmetrical binomial test and the prototype for many other designs, such as AAA-B, AAAA-B . . . , AAA-BB, AAAA-BB . . . , AAAA-BBB . . . , and so forth. As the number of members of one set of samples increases, the variety of test designs also increases and depends upon the number of members in the second set of samples. Selection of a specific design depends upon the size of the panel available, the degree of discrimination desired, and the importance of possible fatigue factors resulting from the testing of many samples.

Although these test systems are binomial in the sense that a single judge may return only one of two possible answers to any one problem, it is necessary to examine the kinds of problems presented to a judge in order to determine the chance probabilities associated with each binomial test system employed.

DIFFERENCE TESTS

Inasmuch as problems concerned with differences are reputed to be least complex, it is logical to begin with

problems of this type. It must be clearly established at the outset that a difference test attempts only to determine whether a difference exists between two samples. The simplest true difference test is exemplified by the triangle test.

For example, two groups of samples are prepared, one of which contains two subsamples, AA, and the other one sub-sample, B. After these are coded and mixed, they are given to a judge with the instruction to divide the three samples correctly, if possible, into two groups. The judge must be informed that two, but only two, different materials are being tested. This kind of information is an essential part of the difference test. The judge is also asked to make a guess with respect to the pair and the odd sample, if he cannot detect a real difference. Answers of "no difference" are not permitted.

The probability that the judge will separate the samples into the correct groups by chance when the sensory differences between the two materials are not great enough to be detected by taste or odor is one-third. This follows from a calculation of the ratio of the number of ways a correct answer can be obtained to the total number of answers possible. It is well known that in this case the total number of answers possible is three, AA-B, AB-A, and BA-A, only one of which, AA-B, is correct.

This brief exposition is necessary to show that it is impossible to carry out a true difference test with a system of only two samples, A-B. A true difference test admits by information given to the judge that the two samples are different. Because answers of "no difference" are not permitted, it is impossible for the judge not to be correct in his separation of the samples into two groups. Both A-B and B-A, the two possible arrangements, are correct. Hence the probability of the judge being correct in this case is one.

In the past a two-sample system has been called a difference test. The question normally asked of the judge has been, "Is there a difference between these two samples?" However, the only answers that can be given by the judge are, "There is a difference" or "There is no difference." Inasmuch as answers of "no difference" are not permitted, the question that accompanies the test is ambiguous and the test an absurdity.

Recently Peryam and Swartz *(8)* have discussed what is called a duo-trio test, which is perhaps intermediate between the A-B and the AA-B tests. It avoids the ambiguity pointed out for the A-B system. Two samples, one an unidentified control and the other an unknown, are compared with an identified control to determine which of the two is different from the identified control. As this test requires an answer ("no difference" answers being unpermissible), a judge can only be either right or wrong. The probability of the judge returning a correct answer (identifying the "different" sample) by chance is clearly one-half.

Before generalization about the probabilities related to binomial tests, one other test system, AA-BB, will be discussed briefly to demonstrate the abnormality of symmetrical systems. It has been shown that for the A-B system, when used as a true difference test, the two possible chance answers A-B and B-A are both correct and the chance probability of a correct answer is one. As shown by the application of the formula for permutations

$$z = \frac{s!}{a!\,b!}$$

where z is the total number of possible answers, s is the total number of samples, and a and b are the numbers of similar samples in each of the two groups, the AA-BB system permits six answers, namely, AA-BB, AB-AB, AB-BA, BA-AB, BA-BA, and BB-AA. An examination of these six answers shows that the first and last answers are both correct, since the four samples have been separated into two groups each containing two similar samples. Therefore, the probability of a judge making a correct separation by chance is one-third (two correct answers divided by a total of six possible answers). The efficiency of this system as a difference test is, therefore, no greater than that of the triangle (AA-B) system. If this analysis were extended to other systems, it would show that all symmetrical systems are similarly inefficient in that an asymmetric test based on a system of fewer samples is equally efficient and that an asymmetric test based on an equal number of samples is more efficient.

The relationship between any one of several test systems and its efficiency is indicated in Table 1, which

TABLE 1

Probability of a judge making a correct separation by chance of s samples into two groups, each containing a and b samples

b	a = 1	2	3	4	5	6
1	1	1/3	1/4	1/5	1/6	1/7
2	....	1/3	1/10	1/15	1/21	1/28
3	....	....	1/10	1/35	1/56	1/84
4	....	....	....	1/35	1/126	1/210
5	....	....	....	....	1/126	1/462
6	....	....	....	....	....	1/462

shows for each system the probability of a judge returning a correct answer by chance. The efficiency of a system is inversely proportional to the probability given.

Any one of the test systems described might be employed to measure the discriminatory ability of prospective members of the so-called analytical test panel. The test system actually employed depends upon the level of sensitivity of a panel member required by the experimenter. If the level of sensitivity is set arbitrarily at 10% (p is 0.10), the simplest test system that can be used is the one composed of a total of five samples, three of one test material being alike and two of the other being alike, AAA-BB. If a 5% level (p is 0.05) is set, a system composed of at least seven samples is required. A system composed of nine samples, AAAAA-BBBB, is the simplest system that will provide a level of sensitvity of 1%. However, it is difficult to think of any test materials that might be presented to a judge in such numbers without resulting in inaccuracy due to fatigue factors.

The probabilities calculated for the systems described have been based on completely correct separation of the mixed samples into two groups each containing similar samples. The situations in which the judge misplaces

two samples, for example, AAAB-ABB or AAB-ABB, require some investigation to determine whether the chance probabilities of such arrangements are equal to or less than 0.05. Analysis of the various responses that can occur in each system demonstrated that in no case will a misplacement of two samples yield a significant result. It follows, therefore, that a single judge must make a completely correct separation of the samples in order for the result to be significant. Although errors might be acceptable if the test systems used contained a greater number of samples than twelve, these systems have little practicability and have not been considered.

QUALITY JUDGMENT TESTS

Binomial test systems may also be employed as the basis for quality judgment. When a quality judgment test is used to determine whether one material is sweeter, more tender, or more aromatic than another, it may be necessary to divide the problems into two parts, first, to determine whether the judge can actually differentiate correctly between the two materials presented and, second, to determine in which direction the assignment of higher quality is made. For a single judge, the part related to discrimination has already been covered.

Any paired comparison test, A-B, is identical with the quality judgment test. The chance probability for this case is one-half, since the judge can make his assignment of quality difference is only one of two ways. Actually this is a combined probability obtained by multiplying together the probability of making a correct discrimination, which is one, and the probability of quality assignment, which is one-half.

The chance probability of quality assignment, or of correct identification, for any one of the binomial systems discussed above may be found readily by multiplying the appropriate probability in Table 1 by one-half. For example, the chance probability for system A-B is one-half, for system AA-B one sixth, and so forth. Only in the cases of symmetrical systems is the total probability equal to the reciprocal of the total number of possible responses. Otherwise the total probability is equal to the reciprocal of twice the total number of possible responses.

The simplest system that will yield a significant result in the hands of a single judge is one of five samples, AAA-BB. A highly significant result ($P<0.01$) may be obtained from a single judge if a system of eight samples, AAAAA-BBB, is used.

Both Fisher*(2)* and Wood *(9)* discussed their problems in terms of quality discrimination rather than true difference. In Wood's paper, the judge is presented with an equal number each of A and of B. The samples are not labelled. The judge is asked not only to separate the A's and the B's, but also to state which group is A and which is B. In the case of Fisher's lady tea expert, the object was not only to separate the eight samples into two groups of four each, but also to identify the group prepared by adding milk to brew or brew to milk. Each of these examples, however, used a symmetrical system. The total chance probability for correct identification in each case is, as shown above, equal only to the reciprocal of the total number of possible responses. None of these systems is as efficient as one comprised of an equal number of samples distributed asymmetrically, such as, AAA-B, AAAA-BB, and the like.

Again it is necessary to consider whether a judge who makes two errors (one pair of misplaced samples) is exhibiting discriminatory ability great enough for the result still to be significant. An analysis similar to one discussed under difference tests shows that if systems contain eleven (a is 6, b is 5) samples, the judge may make two errors and the result will still indicate a significant degree of discrimination. However, simpler systems requiring a completely correct separation of all samples should be more practical for testing purposes.

The test systems discussed provide a means for selecting rapidly prospective panel judges whose sensitivities can be described in terms of probability levels. They provide a means for distinguishing experts from non-experts and for checking the sensitivity of panel members on a day-to-day or week-to-week basis. They provide an excellent means for measuring individual thresholds and discriminatory ability. The range of usefulness and applicability have not yet been explored. In our laboratories a program has been devised to determine more accurately individual thresholds and discriminatory ability with respect to simple taste factors. Other applications will follow and be apparent to those with different specific interests.

REPETITIVE TESTING

The discussion to this point has been limited to responses by a single judge and the probabilities associated with a number of test systems each of which is used only once. If in some cases (as for example, in those in which fatigue may be a factor), the test system may be presented to the judge two or more times. The partial probabilities of completely correct responses from repetitive testing of a single judge may be obtained, as is well known, from expansion of the binomial expression:

$$p = \left(\frac{x}{z} + \frac{y}{z}\right)^n \qquad (1)$$

where p = total probability = 1; x/z is the probability of a single judge making a correct separation by chance; y/z is the probability of a single judge making an incorrect separation by chance; x is the number of correct arrangements possible; y is the number of incorrect arrangements possible, z equals $(x + y)$ which is equal to the total number of arrangements; and n is the number of separate tests taken by the judge.

To simplify calculations, equation (1) may be rewritten in the form

$$p = (1/z)^n\,(x + y)^n \qquad (2)$$

or

$$p = (1/z)^n\left(x^n + nx^{n-1}\,y + \frac{n!}{(n-2)\,!2!}\,x^{n-2}\,y^2 \ldots\right) \qquad (3)$$

If simplification of the fraction x/z in the case of symmetrical systems is taken into consideration, the first term of this expansion (representing the condition that the judge must make a correct separation of the samples) is always $(1/z)^n$. With the aid of Table 1,

the number of test repetitions necessary for a judge to demonstrate a significant or highly significant level of discrimination may be calculated. The AA-B system requires three or five repetitions to satisfy the respective levels of significance, the AAAA-B system only two or three, respectively. However, the same number of samples (five) when presented as system AAA-BB will immediately yield a highly significant result if solved twice corectly. These examples reveal clearly the increase in efficiency afforded by proper selection of test systems.

It is theoretically possible for one judge to repeat a test as many times as the experimenter desires and, as the number of repetitions increases, to obtain significant results even though some errors in separation are made. Data are analyzed by application of the expanded binomial, equation (3), through a sufficiently large number of terms to determine whether the chance of obtaining the observed result or any other more favorable result is equal to or less than the pre-established significance level. To carry out such an extended test would be tedious and obviously difficult to control. Inasmuch as no test of this nature has been reported in the literature, it is impossible to speak of any instance of practical applicability. If this kind of test were ever of use in some special case, the involved calculations would now at least no longer be necessary. The National Bureau of Standards *(7)* has published tables that can be applied to data derived from tests based on binomial systems.

The significance of quality judgment can be tested in a similar manner by applying the principles that have been developed for discrimination.

CONSUMER ACCEPTANCE AND PREFERENCE TESTING

Much of what has been said about difference and quality judgment tests applied equally well to consumer acceptance and preference tests. The latter fall into the same general category and should be discussed together. Both of these tests attempt to predict the reaction, favorable or otherwise, of the general public or of a specific portion of the general public to one product when compared directly with another. On the one hand, members of a consumer acceptance test panel are selected from a large group of prospective consumers. The panel itself is large and selected only to insure its representative character. On the other hand, the preference panel is generally composed of judges who are conveniently available. It is relatively small but so unselected, in sampling terms, it is known as a "chunk" *(1)*. When participating in either one of these tests, the judge is making a complex assessment of the numerous characteristics of each sample. Actually he measures the degree of quality for each characteristic, weighs the relative importance of each, averages the relative merits of all characteristics, and decides which of the two grand averages is the greater.

The consumer acceptance and preference tests may be classified, therefore, as complex quality judgment tests based on an A-B binomial system. The probability of one judge preferring A is one-half, as is the case for the simple quality judgment test already discussed at length. However, little credence can be attached to the response of one judge given once or repeatedly. In either case it is necessary to have as many opinions as may be physically and economically possible or convenient. If the number of judges is extremely large, as in the case of the consumer acceptance test, the combined data are most conveniently tested for significance by chi-square analysis *(3)*, by calculation of the critical ratio *(8)*, or graphically *(6)*. For preference tests in which the number of judges participating lies between twenty and forty-nine, the above tests and the new Bureau of Standards Tables can be used for significance testing. If the panel consists of less than twenty judges, the new tables provide a means for more accurate analysis than does any of the others.

In general, binomial test systems are fundamental tools, some of which have played important roles in the solution of flavor problems. A determination of the utility of others mentioned in this paper must be made to provide industry and research laboratories with further aid in the development of better food for all.

SUMMARY

Two-sample and three-sample test systems have been called difference, discrimination, quality judgment, consumer acceptance, and preference tests. A two-sample system, A-B, should be used only for measuring quality judgment, consumer acceptance, or preference. It cannot be used to determine true difference or to measure discriminatory sensitivity. The three-sample system, AA-B, is the simplest difference or discrimination system. Other systems (as AAA-B, AAA-BB) used for difference or quality judgment testing are more efficient in that fewer judges or fewer tests are required to obtain significant results.

Consumer acceptance and preference tests are identified as complex quality judgment tests of the A-B type.

All these systems may be called binomial systems, because they are composed of two statistical components. All systems are used in accordance with fundamental principles derived from the laws of probability and the binomial theorem.

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Preparation of Stable Frozen Sauces and Gravies[a]

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Study of the effects of a wide variety of conditions and substances (stabilizers, emulsifiers, or thickening agents) has provided basic information on factors that affect the stability of sauces and gravies subjected to freezing or frozen storage conditions. Varying degrees of improvement in stability were obtained with a number of the substances tested but from all considerations the use of waxy rice flour as the thickening agent gave the most satisfactory sauce.

The separation ("weeping" and "curdled" appearance) that develops when sauces and gravies are subjected to freezing or frozen storage is generally regarded by industry and by research workers *(2, 3, 5, 8, 9)* to be an important quality defect, because it tends to reduce consumer acceptance of products such as chicken a la king. Furthermore, since sauces and gravies markedly increase the flavor stability of frozen cooked meat and vegetable dishes by replacing air in the package *(3, 4, 9)*, they are used in a large portion of precooked frozen foods now produced.

Numerous factors and substances have been considered to be of importance in producing a stable sauce. Thus, homogenization has been frequently mentioned in the literature *(3, 9)* and by members of industry as influencing sauce stability; the type of fat used has been considered to be important; stabilizers such as gelatin, gum tragacanth, casein, Irish moss extractive, and gelatinized starch have been suggested as being of potential value in frozen sauces *(5, 9)*; and milk, if used in the formula, was mentioned by one manufacturer as a likely cause of sauce instability. However, very little experimental work has been reported on the relative importance of these factors. No solution to the problem has been reported in the literature, although products on the market exhibit various degrees of the defect.

The work to be reported here is concerned with effects of homogenization, stabilizers, emulsifiers, thickening agents, type of fat and liquid, storage temperature and fluctuating temperature, and temperature of the thawed sauce on the appearance (and liquid separation) of sauces and gravies submitted to freezing. Special attention is given to thickening agents, since this constituent was found to be directly involved in the stability or lack of stability exhibited by sauces and gravies subjected to freezing.

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[b] Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Report of a study made under the Research and Marketing Act of 1946.

FORMULA AND METHODS

The formula of the standard white sauce was as follows:

Ingredient	%
Milk (skim)	90.2
Hydrogenated vegetable oil	4.6
Flour (all-purpose)	4.6
Salt	0.6

When different thickening agents were tested, the amounts of the thickening agent were varied to give sauces of approximately the same thickness as the standard. The amounts of the other ingredients remained constant. The formulas used for chicken or turkey gravy were as follows:

Ingredient	%
Milk (skim) + broth	88.6-92.2
Turkey or chicken fat	3.9- 4.6
Flour or starch	3.4- 6.4
Salt	0.4- 0.6

Preparation and packaging of sauce or gravy. The thickening agent was mixed with the melted fat (Method 1); liquid, warmed to 140° F. (60° C.), was added and mixed thoroughly with the other ingredients; the mixture was heated with constant stirring and cooked for 1 minute after it reached the boiling point; and salt was added during the last 20 seconds of cooking. When the effect of homogenization was to be determined, the sauces were homogenized immediately after cooking. When stabilizers and emulsifiers were tested, they were added according to the directions of the manufacturers.

In a few cases where the effect of cooking method was to be tested or where a smooth sauce could not be obtained by adding the thickening agent to the melted fat, the thickening agent was combined with the cold milk (Method 2). In such cases the cold milk was added gradually to the thickening agent with constant stirring to form a smooth paste. This paste was added to the fat and the entire mixture was heated as in the normal procedure. With a few products, severe lumping occurred even when the milk was added gradually to the thickening agent. In these cases the whole mixture was allowed to stand until the mixture became smooth, sometimes for as long as 3 hours, before the sauce was cooked.

The cooked sauce was weighed into plain "8Z Short" (211 x 300) tin cans, 115 g. of sauce per can. The cans were sealed, frozen in an air blast at —10° F. (—23.5° C.) for 16-17 hours, and then transferred to storage rooms held at various temperatures.

Thawing of frozen sauce was carried out in such a way that the temperature of the thawed sauce was either 70° to 77° F. (21° to 25° C.) or 190° to 212° F. (88° to 100° C.). The lower temperature thawing was accomplished by placing the cans in a water bath at 77° F. (25° C.) for 2 hours. The higher temperature thawing was accomplished by submerging the cans in boiling water for 40 minutes. The cans were weighted to prevent shaking during boiling.

Measurement of thickness of sauces. The thickness of the sauces at 185° F. (85° C.) was measured by using a line spread apparatus (American Instrument Company) to determine the area over which a given amount of sauce will spread. The hot sauce is poured into a greased metal ring in position on the center of a metal plate inscribed with concentric circles. When the plate is lowered, the sauce flows from beneath the ring. Readings are recorded as the number of circles covered; hence

the greater the reading, the greater the area covered, and therefore the thinner is the sauce. A reading of 24-25 corresponds to a sauce of medium thickness.

Stability criteria. Criteria of stability of sauces were, (a) appearance of the sauce as judged by a panel of judges, and (b) liquid separation determined by centrifuging. For appraising or scoring the appearance of the sauces, cans containing the thawed sauces were opened and the contents emptied, without stirring, into 150 x 20 mm. petri dishes. In the early tests samples were judged only for appearance on a scale ranging from 1 to 10, with a score of 1 indicating the minimum degree of smoothness (a very watery or curdled sauce) and a score of 10 indicating the maximum degree of smoothness. In later tests the score sheet for appearance was modified to provide for separate scoring of texture, separation, and smoothness. Texture was rated 10 when it was the "short" texture typical of white sauce, gravy, or cornstarch pudding; it was rated 0 when it was the gelatinous, "long" texture typical of tapioca pudding. Separation was rated 10 when no watery phase was evident and 0 when the sauce was curdled and showed much separation. Smoothness was rated 10 when the sauce had no perceptible unevenness of texture, 0 when it was lumpy.

For the centrifuge test sauces were thoroughly mixed by stirring in order to obtain uniform samples. If the sauce had been thawed in the boiling water bath, it was cooled before mixing. Two 50-g. samples were weighed into plastic centrifuge tubes and centrifuged for 20 minutes on a Sorval Angle Centrifuge. Liquid that separated during centrifuging was filtered through Whatman No. 1 filter paper. The appearance of the filtrate was noted, the amount was determined, and the percentage of liquid separation was calculated.

RESULTS AND DISCUSSION

The instability of standard white sauce. Data from several lots of standard sauce prepared for different experiments have been combined to give a picture of the effect of freezing, storage time, and storage temperature on the standard sauce (Figure 1). This data is useful as a base for estimating the improvement in stability of sauces treated with various thickening agents or added stabilizers.

Some liquid separation occurs on centrifuging the sauce even before it is frozen. The amount of separation in the sauce is greater if the sauce has been frozen and is still greater if it has undergone frozen storage. For any given storage period, the amount of separation is greater the higher the storage temperature. Visual examination of the sauces after thawing revealed a clear liquid phase and an opaque phase that had a curdled appearance (Figure 2). Separation of the sauces thawed at 77° F. (25° C.) is not prevented by increasing the thickness of the sauces. In sauces whose consistency varied from thick to thin (line spread reading 22-28), the percent of liquid separation varied only from 51 to 56 after 5 weeks of storage at 10° F. (—12° C.).

Heating the sauces decreased the amount of liquid separation obtained in the centrifuge test, even though the sauces were cooled to room temperature for the test. For example, liquid separation was 37 and 57% for products thawed at 77° F. (25° C.) after 5 weeks at 0° and 20° F. (—18° and 6.5° C.) but was reduced to 9 and 13% for corresponding samples that had been heated to approximately 200° F. (93° C.). Also, the appearance of the heated sauces was improved—the remaining defect was a lack of smoothness or presence of a slightly curdled effect rather than separation of liquid as found in the thawed sauces.

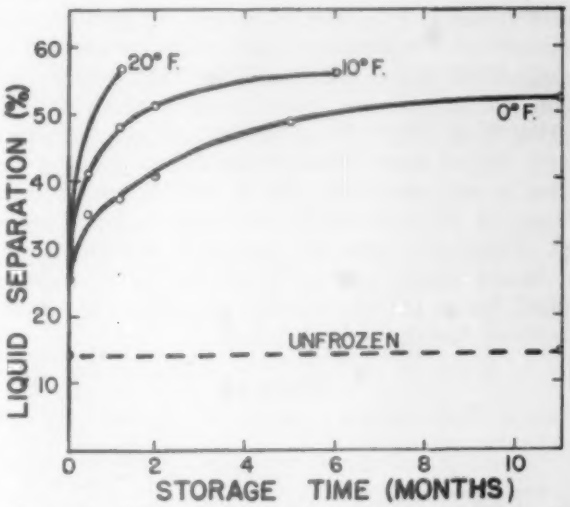

FIGURE 1. Effect of storage time and temperature on liquid separation of standard white sauce thawed at 77° F. (25° C.).

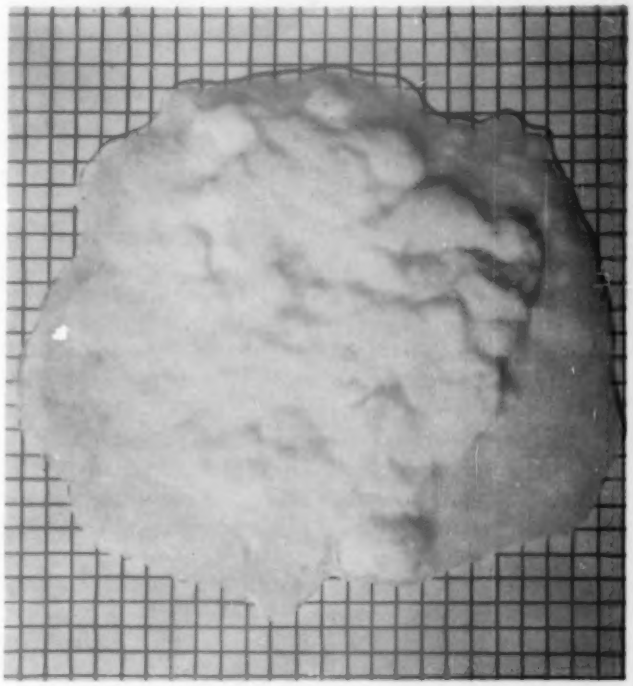

FIGURE 2. Standard white sauce thickened with wheat flour, stored at 0° F. 5 months, thawed at 77° F. (25° C.).

In contrast with the liquid separation for sauces thawed at 77° F. (25° C.) and not further heated, the amount of liquid separation of the sauces after heating is affected by the thickness of the sauce. After storage for 5 weeks at 10° F. (—12° C.) a thick, a medium, and a thin sauce (5.5, 4.6, and 3.7% flour; line spread readings of 22, 24, and 28) showed liquid separations of 3, 15, and 24%. The thick sauce had the somewhat curdled appearance typical of the ordinary sauce.

Effect of homogenization on stability of standard white sauce. Homogenization of the standard white sauce eliminated liquid separation from unfrozen sauces. It also caused a slight decrease in the amount of liquid separation that appeared after freezing and after storage at 0° F. (—18° C.), but there was no statistically significant difference in the appearance of the thawed

sauces (Table 1). The data for appearance were obtained by comparison with freshly prepared, unhomogenized sauces that had been refrigerated overnight. These unfrozen, coded controls received scores ranging from 8.6 to 9.1 at the various storage periods tested. When sauces homogenized before freezing were heated to approximately 190° F. (88° C.) after frozen storage (0° F., 11 months), there was no liquid separation. There was some improvement in smoothness of the heated sauce, compared with the unhomogenized control, but as the sauce cooled slightly the appearance resembled that of the heated control.

TABLE 1

Effect of homogenization on stability of standard white sauce

Storage time at 0° F.	Liquid separation of sauce thawed at 77° F.		Appearance score[e] for sauce thawed at 77° F.[d]	
	Homogenized	Unhomogenized	Homogenized	Unhomogenized
months	%	%		
0 (unfrozen)	0	14	9.2	8.3
0 (frozen)	7	25	4.7	6.1
0.5	27	35	3.0	3.2
2	35	41	3.6	2.2
5	40	49	2.8	2.2
11	48	51	2.7	2.0

[e] 10 represents smooth, no separation; 1 represents curdled, much separation.

[d] Sauces thawed at 77° F. reached a temperature of approximately 70° F.; sauces thawed at 212° F. reached a temperature of approximately 190° F.

To determine whether homogenizing at various times affects stability, sauces were homogenized (a) immediately after cooking, (b) after holding at 35° F. (1.5° C.) overnight, and (c) after freezing at —10° F. (—23.5° C.) overnight, followed by thawing. The sauces were frozen and held at 10° F. (—12° C.) for 3 months. Tests on liquid separation conducted at monthly intervals showed no advantage of any of the three treatments over the others. After three months the liquid separation of all of the samples was within a range of 47 to 56%.

Screening of available stabilizers, emulsifiers, and thickening agents. Various stabilizers were tested to determine whether their ability to hold water and retard ice crystal growth in products such as ice cream would be effective in stabilizing sauces submitted to freezing. Emulsifiers were tested to determine whether their tendency to prevent separation of fat and liquid phases would help yield stable sauces and gravies. Thickening agents other than wheat flour were tested to determine whether their composition, particularly in the size or degree of branching of the starch molecules, could affect the behavior of frozen sauces. Some 60 substances were screened by determining the amount of liquid separation that occurred on thawing sauces containing these substances. The sauces were held in frozen storage at 10° F. (—12° C.) for 1 to 2 months.

Very few of the commercial stabilizers or emulsifiers added to the standard white sauce had a beneficial effect in retarding liquid separation from the sauces thawed at 77° F .(25° C.) (Table 2). The greatest reduction in percentage of liquid separation was obtained by the addition of 1.5% gelatin. The addition of 1% citrus pectin reduced liquid separation only slightly, but it had

TABLE 2

Effect of stabilizers and emulsifiers on liquid separation of thawed standard sauces. Frozen storage of 1-2 months at 10° F.

Stabilizers and emulsifiers	Concentration of stabilizer or emulsifier	Liquid separation[g]	
		77° F. thaw	212° F. thaw
	%	%	%
Standard sauce (no additive)	....	49-56	14
Glycerol monolaurate	0.1, 0.2	36-42	....
Same, but with sauce homogenized	0.1	45	....
Glycerol monomyristate	0.1, 0.2	23-49	9
Same, but with sauce homogenized	0.1	42	....
Glycerol monopalmitate	0.1, 0.2	44-51	....
Glycerol monostearate	0.025-0.3	38-50	8
Same, but with sauce homogenized	0.1	44	....
Stearoyl glycine	0.002-0.1	33-39	....
Polyoxyethylene stearate	0.05-0.2	36-41	....
Sorbitan monolaurate (Span 20)[e]	0.5	24-46	10
Polyoxyethylene sorbitan monolaurate (Tween 20)[e]	0.5	48	....
Sorbitan monostearate (Span 60)[e]	0.1, 0.5	45-57	....
Polyoxyethylene sorbitan monostearate (Tween 60)[e]	0.5	49-51	....
Sorbitan monooleate (Span 80)[e]	0.5	48-50	14
Polyoxyethylene sorbitan monooleate (Tween 80)[e]	0.5	44	....
Polyoxyethylene sorbitan tristearate (Tween 65)[e]	0.5	52	....
Span 20 and Tween 20	0.25 + 0.25	45	....
Span 20 and Tween 60	0.13 + 0.37	42	....
Span 20 and Tween 80	0.13 + 0.37	43	....
Span 60 and Tween 60	0.37 + 0.13	49-53	....
Same	0.25 + 0.25	43-50	....
Same	0.13 + 0.37	48-50	....
Span 80 and Tween 80	0.37 + 0.13	51	....
Same	0.25 + 0.25	50	....
Same	0.13 + 0.37	49	....
Citrus pectin (218 Grade, S. S.)	0.25, 0.5	48-53	....
Same	1.0	36	11
Gelatin (Swift and Co., Velvetex)	0.5	37-41	19
Same	1.0	25	....
Same	1.5	0-9	23
Gelox (Swift and Co.)[f] sauce homogenized	0.5, 1.0	34-38	0
Gelsoy (N.R.R.L., prep. at Allied Mills)[f]	1.0, 1.5	58-65	....
Kelcoloid (Kelco Co.)[f]	0.2, 1.0	51-53	....
Same	0.1	50	12
Same	1.0	23	0
Krim Ko Gel Light (Krim-Ko Corp.)[f]	0.1	34	....
Krim Kold (Krim-Ko Corp.)[f]	0.1, 0.2	23-44	....
Sta-Vel (American Foods Labs.)[f]	0.3	47	....
S-233 (American Food Labs.)[f]	0.2, 0.4	43	....
Same, but with sauce homogenized	0.4	43	....
Sure-Bet (National Pectin Products Co.)[f]	0.1, 0.2, 0.3	52-57	....
Vesterine (Swift and Co.)[f], with sauce homogenized	0.5, 1.0	38-45	0

[e] Atlas Powder Co.

[f] Gelsoy, soybean protein derivative; Kelcoloid, organic derivative of alginic acid; Kelcosol, a fibrous form of sodium alginate; Sta-Vel, blended, modified, specially processed gums; S-233, Cellulose gum, refined extract carageen, emulsifying agents; Krim Ko gel Light, extra strong extractive from sea weed related to Irish moss; Krim Kold, extractive from sea weed related to Irish moss; Sure-Bet, pectin and locust bean gum, Vesterine, gelatin, mono and diglycerides; and Gelox, mono and diglycerides, sodium carboxymethyl cellulose, dextrose, carrageenin, gelatin.

[g] Sauces thawed at 77° F. reached a temperature of approximately 70° F.; sauces thawed at 212° F. reached a temperature of approximately 190° F.

an additional beneficial effect in that sauces containing the pectin required a minimum of stirring to regain a desirable smooth appearance.

After storage for 1-2 months at 10° F. (—12° C.), sauces thickened with the common starches and flours showed approximately the same amount of separation on thawing at 77° F. (25° C.) as occurred in the standard sauce (Table 3). Of the chemically modified starches, a corn starch (R-9) prepared by a carboxymethylation reaction to achieve a fairly high (0.40-0.55) degree of substitution was outstanding in that it showed no liquid separation when thawed. Of the waxy cereals,

waxy rice flour and waxy rice starch were considerably more stable than the others.

When sauces thickened with common starches and flours were thawed and heated to 190° F. (88° C.) after 1-2 months in frozen storage, there was less liquid separation than in the sauces that were thawed at 77° F. (25° C.) (Table 3). When sauces containing stabilizers and emulsifiers were so treated, the liquid separation was eliminated in some cases; in others it was greater than the amount in the sauces that were not heated (Table 2). Sauces thickened with waxy cereals consistently showed no separation after heating (Table 3).

The correlation between the percent liquid separation and the appearance of the sauces thawed at 77° F. (25° C.) was usually good. When appearance was scored, whenever liquid separation was greater than 15% the scores were 5.0 or less (with one exception, see Table 1). The correlation between percent liquid separation and the appearance of the heated sauces varied with the type of thickening agent and the presence of stabilizers or emulsifiers. Heating of the sauces containing the common starches or flours caused the same type of improvement in appearance that was found in heating of the standard sauce. The clear liquid usually disappeared but a somewhat curdled appearance remained in the opaque phase. This curdled appearance remained even in the cases where the liquid separation in the centrifuge test was eliminated. Sauces thickened with common rice starch or flour, however, seemed somewhat less curdled than those thickened with the other common cereals. When stabilizers and emulsifiers were used, the heated sauces showing no liquid separation by the centrifuge test were not necessarily smoother in appearance than those showing 10-25% separation. When the stored sauces thickened with the waxy cereals were thawed and heated, their appearance could not be distinguished from that of freshly prepared sauces containing the same thickening agents.

All of the sauces containing the waxy starches had a "long" texture that would not be desirable in a white sauce or gravy; the sauce thickened with the available sample of waxy sorghum flour and with the modified corn starch R-9 also had a "long" texture. However, the sauces thickened with our one sample of white waxy corn flour and with waxy rice flour had a desirable "short" texture and were unusually smooth. The only available sample of white waxy corn flour was prepared from grain stored under refrigeration for 5 years at the Northern Regional Research Laboratory. In evaluating the tests with this sample the possibility must be considered that the long storage influenced those properties of the grain that determine whether the flour will produce a "long" or "short" texture sauce.

The results of these screening tests led us to select flours and starches from waxy cereals for more thorough study.

Effect of storage at 0° F. (—18° C.) on stability of sauces and gravies made with waxy cereal products. Sauces thickened with waxy rice flour and stored for 5 months at 0° F. (—18° C.) showed no liquid separation after thawing (Table 4 and Figure 3), and after 11 months the separation was slight. Sauces containing ⅗ waxy rice flour and ⅖ wheat flour showed little separation after 5 months at 0° F. (—18° C.) particularly when the sauce was homogenized before freezing. Starches thickened partially or wholly with waxy rice flour showed considerable thinning when homogenized. Those containing the waxy corn starch showed greater separation, and, as mentioned previously, had the "long" paste character.

In addition to the liquid separation measurements the appearance of the thawed sauces was judged at each storage period. Two unfrozen, coded controls were scored at the same time as the experimental samples. One control was thickened with wheat flour and the other with waxy rice flour. Both were prepared the day before examination and refrigerated overnight. Scores for the waxy rice flour controls ranged from 9.5 to 10.0 at the various judging periods; those for the wheat flour controls ranged from 8.6 to 9.1. The results show that unhomogenized waxy rice flour sauce is more smooth in appearance than a mixture of waxy rice flour and wheat flour sauce or waxy corn flour sauce. On the other hand, the homogenized mixed flour sauce is much improved compared with the standard sauce (Table 1).

TABLE 3

Liquid separation on thawing sauces, thickened with various starches and flours. Frozen storage: 1-2 months at 10° F.

Thickening agent	Thickness of sauce (line spread)	Liquid separation [1]	
		77° F. thaw	212° F. thaw
		%	%
Common cereal flours:			
Rice, RF8-80 mesh (WRRL)	21-23	36-55	14
Wheat (Gold Medal, General Mills, Inc.)	22	51	3
Same	24-25	54	14-15
Same	28	56	24
Common cereal starches:			
Canna (NRRL, 6520-1584-12)	22	58-62	6
Corn, small granule (Clinton Industries), Kingsford's (Corn Products Refining Co.), NRRL (Composite of Nos. 3920, 2734, 4182)	24	46-61	21
Dasheen (NRRL, 4242-1582-26)	28	59-64	15
Pea, wrinkled	No thickening	....	....
Pea, smooth	24 (ca.)	50	21
Potato (Idaho Potato Starch Co.), (NRRL, 6352-1584-10)	23-24	50-65	....
Same	21 (ca.)	41	0
Rice, Colusa (NRRL, 1919-1582-45)	23	45-50	0-14
Sago	24	50-56	4
Sorghum, Hegari, Martin Milo (NRRL)	22-23	49-63 [b]	13-19
Sweet potato (SRRL, K-46-1-15)	22	53	10
Tapioca	21-26	31-53	0
Modified starches:			
Corn, No. 3051, 10-fluidity acid modified (Corn Products Ref. Co.)	22	57 [j]	....
Corn, 20-fluidity acid modified (NRRL, CD-7532)	26	32	....
Corn, 60-fluidity acid modified (Corn Products Ref. Co.)	30	27-37	....
Corn, RX 12G-2 (National Starch Products Co.)	20	37	....
Corn, 4101 Thick boiling (Corn Products Ref. Co.)	25	58-61 [b]	....
Corn, Carboxymethyl, R-10 (Corn Products Ref. Co.)	25 (ca.)	70	....
Corn, Carboxymethyl (degree of substitution: 0.40-0.55) R-9 (Corn Products Ref. Co.)	24 (ca.)	0	0
Corn, XR32 Hydroxypropyl (Corn Products Ref. Co.)	22 (ca.)	51	1
Wheat, Thick boiling, A-22 R3E-547 (General Mills)	23	58 [j]	....
Wheat, B-2420, R3E-317 (General Mills)	24-25	32-39 [b]	....
Wheat, B-2475, R3E-396 (General Mills)	28	32 [j]	....
Waxy cereal flours:			
Corn, white (NRRL-7625F)	25	38-50 [b]	0
Rice, Mochi Gome (Rice Products Co.)	24	0-26 [b]	0
Sorghum (Grain Products Inc.)	28	51-59	0
Waxy cereal starches:			
Corn, WM42, Iowax 1 (NRRL)	21-22 (ca.)	17-55	0
Corn, Amioca, Clear Gel (National Starch Products)	22-26	49-63	0
Corn, white (NRRL 7625-3113-191)	25	48 [j]	0
Rice, Mochi Gome	22	37 [j]	0
Rice (NRRL 3872-1581-4)	28	4-10 [b]	0
Sorghum (Hubinger Co.)	25	45-59 [b]	0

[b] Cooked by methods 1 and 2.

[1] Sauces thawed at 77° F. reached a temperature of approximately 70° F.; sauces thawed at 212° F. reached a temperature of approximately 190° F.

[j] Cooked by method 2 only.

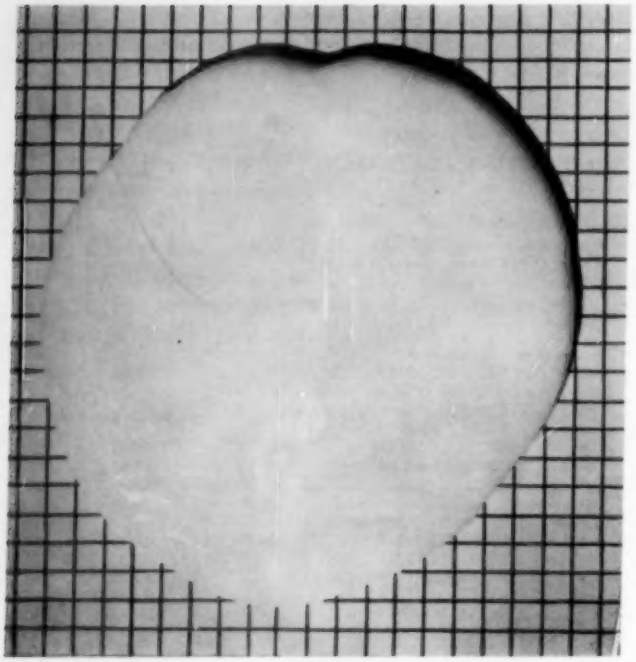

FIGURE 3. White sauce thickened with waxy rice flour, stored at 0° F. 5 months, thawed at 77° F. (25° C.).

Turkey and chicken gravies, prepared with poultry fat and with broth substituted for part of the milk, have shown stabilities similar to that of white sauce. After 8 months of storage at 0° F. (—18° C.), gravies thickened with waxy rice flour showed little or no separation after thawing; those thickened with wheat flour or waxy corn starch showed the curdled appearance and liquid separation found in white sauces thickened with those products. The behavior of the thickening agents in the various products indicates that they, rather than the fat or liquid, are the ingredients primarily responsible for differences in frozen storage stability.

TABLE 4

Effect of homogenization and storage at 0° F. on stability of sauces thickened with waxy cereals

Storage time at 0° F.	Thickening agent				
	Waxy rice flour (unhomogenized)	Waxy rice flour (⅓), and wheat flour (⅔)		Waxy corn starch	
		(homogenized)	(unhomogenized)	(homogenized)	(unhomogenized)
a. Percentage liquid separation of sauce thawed at 77° F.[k]					
months					
0 (unfrozen)	0	0	0	0	0
0 (frozen)	0	0	0	0	0
0.5	0	1	2	0	9
2	0	1	6	3	23
5	0	4	11	22	32
11	6	21	26	45	49
b. Appearance score for sauce thawed at 77° F.[k]					
0 (unfrozen)	9.5	9.9	9.4	10.0	6.8
0 (frozen)	9.4	9.8	9.3	7.2	8.1
0.5	9.3	10.0	8.6	6.4	6.7
2	9.3	8.8	6.0	6.0	4.6
5	9.4	8.4	5.0	4.3	3.7
11	8.3	4.9	4.1	[l]	[l]

[k] Sauces thawed at 77° F. reached a temperature of approximately 70° F., sauces thawed at 212° F. reached a temperature of approximately 190° F.

[l] Gelation of thawed sauces prevented adequate judging of appearance.

Attempts to relate stability differences found for sauces made with common and waxy cereals to known properties of the cereal components. The difference between common and waxy cereals is, of course, primarily a difference in the starch fraction of the two cereals. Starches from common cereals contain approximately 23-28% by weight of components exhibiting the properties of linear polymers, while those from waxy cereals contain less than 1% of these unbranched starch chains, which have been designated amylose. The remaining component of the starch in each case is the branched fraction, called amylopectin. The potential significance of these differences for frozen sauces and gravies can be recognized from the following comments of Kerr *(6)*:

"Solutions of starch which have aged at room or lower temperatures undergo the phenomenon of retrogradation. A part of the starch aggregates progressively, and finally forms an insoluble microcrystalline precipitate. . . . The retrogradation process may be hastened by freezing aqueous solutions; in this way, ordinarily stable solutions may be forced to retrograde. Although some amylopectin preparations have a tendency to retrograde from solution, the property is greatly exaggerated in pure amylose solutions." Thus, the common starches containing the unbranched molecules might be expected to retrograde and eliminate water more rapidly from the sauces than the waxy starches.

However, all amylopectins or waxy starches are not the same. For example, Bates, French, and Rundle *(1)* report that amylopectins from different starches do not behave alike in the iodine titration. As far as was tested, it appeared that the more highly branched the amylopectin, the less was its affinity for iodine. Of the polysaccharides tested, glycogen had the least affinity for iodine, followed by waxy rice, waxy corn, waxy barley starch, and potato and corn amylopectin. Meyer and Fuld *(7)* also report that the degree of branching of waxy rice starch is between that of ordinary amylopectins and of glycogen, and that the waxy rice starch molecules are of low and intermediate molecular weights.

The following results indicate that much of the differing behavior of the starches and flour in sauces and gravies can be attributed to these rather well-recognized differences in the starches.

A comparison of sauces thickened with starch from the common and waxy varieties of corn, sorghum, and rice, and with ordinary and waxy rice flour showed in each case that the sauces containing starch or flour from the waxy varieties were considerably more stable to freezing than those containing the common varieties (Table 5). However, liquid separation in the sauces thawed at 77° F. (25° C.) was found after shorter frozen storage times in sauces containing the waxy corn and and sorghum starches than in sauces containing waxy rice starch or flour. These two results may reflect respectively (a) the greater amount of branched molecules in the waxy cereals than in the common cereals, and (b) the variation in molecular size and degree of branching of different waxy cereal starches.

Sauces thickened with the starch from waxy corn and with the amylopectin fraction of common corn starch gave essentially the same amounts of liquid separation after freezing and after storage at 10° F. (—12° C.) for periods up to 6 months. Similarly when a starch mixture consisting of 78% amylopectin and 22% amylose was used, it made no difference in the amount of liquid separation whether the amylopectin was waxy corn starch or was from common corn starch. These results support the view that the difference between the common and waxy varieties depends on the presence of the amylose fraction in the common starch.

A slight decrease in the amount of liquid separation in the sauces thickened with corn and sorghum starches was noted after storage for 6 months (Table 5), and a similar phenomenon was noted after prolonged storage of many of the products

TABLE 5

Stability of sauces prepared from starches and flours of common and waxy cereals

Storage time at 10° F.	Rice				Corn		Sorghum	
	Starch		Flour		Starch		Starch	
	Common [m]	Waxy [n]	Common [o]	Waxy [p]	Common [q]	Waxy [r]	Common [s]	Waxy [t]
a. Percentage liquid separation in sauces thawed at 77° F.[w]								
months								
0 (frozen, unstored)	23	0	11	0	50	0	44	0
0.5	30	0	29	0	63	21	58	46
2	45	4	43	0	56	49	58	52
6	....	50	54	46	54	43	54	49
b. Appearance score[v] for sauces thawed at 77° F.[w]								
0	....	9.2	9.1	10.0	1.7	9.8	2.4	8.5
0.5	....	8.7	4.3	9.5	1.5	5.0	2.4	2.0
2	....	8.0	1.2	9.8	....[u]	....[u]	....[u]	....[u]
6	....	1.3	1.7	2.5	....[u]	....[u]	....[u]	....[u]

[m] Colusa (N.R.R.L., 1919-1582-45). [n] (N.R.R.L., 3872-1581-4). [o] (RF8-80 mesh, W.R.R.L.). [p] Mochi Gome (Rice Products Co.). [q] Kingsford's (Corn Products Ref. Co.). [r] Amioca (National Starch Products). [s] Hegari and Martin Milo (N.R.R.L.). [t] (Hubinger Co.). [u] Gelation in thawed sauces interfered with judging, as no provision had been made for it on the scoring scale. [v] 10 represents smooth, no separation; 1 represents curdled, much separation. [w] Sauces thawed at 77° F. reached a temperature of approximately 70° F.; sauces thawed at 212° F. reached a temperature of approximately 190° F.

tested. It was associated with gelation of the sauces and also with development of an appearance after thawing described by the judges as resembling fish flakes.

The difference between common and waxy cereals is also apparent in the behavior of the sauces that are heated to approximately 190° F. (88° C.) after being subjected to frozen storage. It has been reported that the association between amylopectin molecules with splitting out of water is more readily reversible than the association between the amylose molecules *(2)*. It therefore appears probable that heating of the sauces causes breaking of the linkages between amylopectin molecules and permits reassociation between them through water molecules.

Heating of the sauces thickened with the common cereals partially eliminates liquid separation (Tables 3, 6, 7, 8, 9) and partially restores the original appearance. However, heating of sauces thickened with waxy cereals completely eliminates liquid separation under all conditions tested, even when the amount of separation in the sauce thawed at 77° F. (25° C.) is greater than 50% (Tables 3, 6, 7, 8, 9). The separation is eliminated whether the sauce is (1) thawed slowly to room temperature and then heated, or (2) thawed and heated rapidly in a boiling water bath. These heated sauces do not differ in appearance from those that have never been frozen.

The complete reversibility, under all conditions tested, of the reactions involved in liquid separation of sauces thickened with waxy cereals and the partial reversibility in those thickened with wheat flour appears to be related to the amylopectin content of the starch. It is interesting to note that in the cases where the thickening agent was a mixture of 40% waxy rice flour and 60% wheat flour, the liquid separation was completely reversed on heating rather than reversed in proportion to the amounts of wheat and waxy rice flours. The amylopectin of the rice flour apparently was able to recombine not only with the water lost by the rice flour during storage but also with the water lost by the wheat flour. A difference between the amylopectin fractions of wheat and waxy rice is, therefore, indicated in addition to the difference between the flours in amylopectin content.

TABLE 6

Effect of storage temperature on stability of frozen sauces after five weeks storage

Thickening agent	Storage temperature, °F.		
	20	10	0
a. Percentage liquid separation of sauces thawed at 77° F.[x]			
Waxy rice flour	48	0	0
Waxy rice flour (3/5); wheat flour (2/5)	45	27	0
Waxy rice flour (2/5); wheat flour (3/5)	45	37	0
Wheat flour	57	49	37
Wheat flour and 1% citrus pectin	39	36	8
R-9 modified cornstarch	0	0	0
b. Percentage liquid separation of sauces thawed at 212° F.[x]			
Waxy rice flour	0	0	0
Waxy rice flour (3/5); wheat flour (2/5)	0	0	0
Waxy rice flour (2/5); wheat flour (3/5)	0	0	0
Wheat flour	13	15	9
Wheat flour and 1% citrus pectin	12	11	8
R-9 modified cornstarch	0	0	0

[x] Sauces thawed at 77° F. reached a temperature of approximately 70° F.; sauces thawed at 212° F. reached a temperature of approximately 190° F.

Character of sauces prepared from the starch and flour of waxy cereals. Starch from white waxy corn and waxy rice, like the amylopectin from ordinary cereals, yields sauces and gravies with a long paste character. As already noted the sauces made with these waxy cereal flours have a short paste character. Yet addition of the protein fraction separated from the cereal during starch preparation failed to influence the long paste character of the sauces made with the starch, thus indicating that either (1) the starch was altered during processing, (2) the protein was altered during process, or simply that (3) the remixing of the separated fraction does not yield a condition similar to that existing in the untreated flour.

Tests were carried out on two batches of sauce from each of the three waxy corn and rice thickening agents (flour, starch, starch + protein).[hh] (In order to cause the protein fraction to go into solution all sauces in this series were prepared by adding the starches, flours, and protein fractions to the cold milk rather than to the melted fat.) Results of liquid separation data showed superiority of waxy rice over waxy corn products but no consistent differences among the three treatments compared within each cereal, indicating that the starch is the fraction responsible for the stability. In this study all of the waxy corn samples thawed at room temperature showed liquid separated after 2 weeks and the waxy rice samples after 2 months of storage at 10° F. (−12° C.).

The effect of a wide range of conditions on the stability of sauces made with waxy rice flour, wheat flour, mixtures of wheat and waxy rice flour, wheat flour plus pectin, and the substituted starch, R-9. The conditions selected for these stability studies include those that might be encountered in commercial processing, storage, or transportation. The processing variable tested was the method of combining the thickening agent with the other ingredients of the sauce, and this

[hh] These fractions were prepared for us by Dr. M. M. MacMasters of the Northern Regional Research Laboratory, Peoria, Illinois.

TABLE 7

Effect of fluctuating storage temperature (0°-20° F.) on stability of frozen sauces

Thickening agent	Number of fluctuating temperature cycles[y]				Storage time and temperature after 3 fluctuating cycles			
	0[z]	1	2	3	2 weeks at 0° F.	2 weeks at 10° F.	2 weeks at 20° F.	2 months at 0° F.
a. Percentage liquid separation of sauces thawed at 77° F.[zz]								
Waxy rice flour	0	0	0	0	0	0	38	0
Waxy rice flour (3/5); wheat flour (2/5)	0	0	0	0	0	21	42	11
Waxy rice flour (2/5); wheat flour (3/5)	0	0	13	31	27	37	38	36
Wheat flour and 1% citrus pectin	0	18	28	36	35	40	35	38
R-9 modified cornstarch	0	0	0	0	....	....	....	....

[y] One cycle equals 48 hrs. at 20° F. followed by 1 week at 0° F.
[z] Tested immediately after freezing in air blast at —10° F.
[zz] Corresponding samples thawed at 212° F. showed no liquid separation except for the wheat flour plus 1% pectin sample, which showed a separation that varied randomly from 9 to 16% (cf. Table 8).

TABLE 8

Effect of fluctuating storage temperature (0°-10° F.) on stability of frozen sauces

Thickening agent	Number of fluctuating temperature cycles[cc]				Storage time and temperature after 3 fluctuating cycles			
	0[bb]	1	2	3	2 weeks at 0° F.	2 weeks at 10° F.	2 weeks at 20° F.	2 months at 0° F.
a. Percentage liquid separation of sauces thawed at 77° F.[dd]								
Waxy rice flour	0	0	0	0	0	0	20	0
Waxy rice flour (3/5); wheat flour (2/5)	0	0	0	0	0	1	38	0
Waxy rice flour (2/5); wheat flour (3/5)	0	0	0	0	0	28	39	10
Wheat flour	20	34	34	41	39	45	49	46
Wheat flour and 1% citrus pectin	0	0	19	10	23	33	37	23
R-9 modified cornstarch	0	0	0	0	0	0	0	0
b. Percentage liquid separation of sauces thawed at 212° F.[dd]								
Waxy rice flour	0	0	0	0	0	0	0	0
Waxy rice flour (3/5); wheat flour (2/5)	0	0	0	0	0	0	0	0
Waxy rice flour (2/5); wheat flour (3/5)	0	0	0	0	0	0	0	0
Wheat flour	9	12	13	13	14	13	12	11
Wheat flour and 1% citrus pectin	9	17	14	11	15	16	11	12
R-9 modified cornstarch	0	0	0	0	0	0	0	0

[bb] Tested immediately after freezing in air blast at —10° F.
[cc] One cycle equals 48 hrs. at 10° F. followed by one week at 0° F.
[dd] Sauces thawed at 77° F. reached a temperature of approximately 70° F., sauces thawed at 212° F. reached a temperature of approximately 190° F.

TABLE 9

Effect of thawing and refreezing on stability of frozen sauces

Thickening agent	Number of thawing-refreezing cycles[ee]				Storage time and temperature after 3 thawing-refreezing cycles			
	0[ff]	1	2	3	2 weeks at 0° F.	2 weeks at 10° F.	2 weeks at 20° F.	2 months at 0° F.
a. Percentage liquid separation of sauces thawed at 77° F.[ff]								
Waxy rice flour	0	0	0	0	0	0	42	0
Waxy rice flour (3/5); wheat flour (2/5)	0	0	0	0	1	36	48	16
Wheat flour and 1% citrus pectin	0	11	27	31	32	37	40	33
R-9 modified cornstarch	0	0	0	0	0	0	0	0
b. Percentage liquid separation of sauces thawed at 212° F.[ff]								
Waxy rice flour	0	0	0	0	0	0	0	0
Waxy rice flour (3/5); wheat flour (2/5)	0	0	0	0	0	0	0	0
Wheat flour and 1% citrus pectin	3	3	12	7	13	10	13	14
R-9 modified cornstarch	0	0	0	0	0	0	0	0

[ee] One cycle equals thaw at 40° F., 24 hours, followed by 1 week at 0° F.
[ff] Sauces thawed at 77° F. reached a temperature of approximately 70° F.; sauces thawed at 212° F. reached a temperature of approximately 190° F.
[ff] Tested immediately after freezing in air blast at —10° F.

variable was given a limited test with a number of the waxy cereals in addition to more complete tests with waxy rice flour. In one cooking method the flour was mixed with the melted shortening; in the other it was mixed with the cold milk. Sauces containing waxy rice flour made by both methods have been frozen at different rates (—10° F. in air blast and 0° F. in still air) and stored at 10° F. (—12° C.) and 0° F. (—18° C.). No differences in stability related to cooking method have been found.

The storage conditions tested include (a) storage for 5 weeks at 0°, 10°, and 20° F.; (b) three fluctuations in temperature from 0° to 20°; (c) three fluctuations in temperature from 0° to 10°; (d) three complete thawings with refreezing at 0° F.; (e) three partial thawings with refreezing at 0° F.; (f) three fluctuations in temperature from 0° to —61° F. (—52° C.), the temperature of dry ice. Each of the above treatments from (b) to (f) was followed by storage for 2 weeks at 0°, 10°, and 20° F. and 2 months at 0° F.

The thawed sauces thickened with R-9 showed no liquid separation under any of the above conditions (Tables 6, 7, 8, 9, part a). The sauces thickened with waxy rice flour showed

separation only when the storage treatment included storage at 20° F. (—6.5° C.). Sauces thickened with wheat flour showed progressive increase in separation with increase in storage temperature and with increase in number of fluctuating temperature cycles. Sauces thickened with mixtures of waxy rice and wheat flour showed separation in amount and time of occurrence intermediate between that of the wheat flour and the waxy rice flour sauces. Sauces containing wheat flour and 1% pectin showed less liquid separation than those containing wheat flour alone, and, as was noted on the screening test with citrus pectin, the separation disappeared with less stirring than was required for the wheat flour sauces. Results obtained following the partial thawing series have not been included because they were very similar to those obtained with complete thawing, the liquid separation being only slightly less in all cases. Likewise, the results for the dry ice series have not been included, since separation was negligible in all cases except for sauces thickened with wheat flour, and in those it was slightly less than the amounts obtained for those samples submitted to temperature fluctuation from 0° to 10° F. (—18° to —12° C.).

Commercial test of waxy rice flour in chicken a la king. Waxy rice flour as a thickening agent for precooked frozen chicken à la king has been given a limited test under commercial conditions.[11] The product contained chicken broth, chicken meat, milk, flour, green peas, green peppers, pimientos, mushrooms, salt, and spices. Sauce for the product was prepared by a batch process in steam-jacketed kettles, and a control lot was prepared using soft wheat flour for the thickening agent. The sauces were added to diced chicken, packaged in a waxed carton with a heat-sealed waxed paper overwrap, and frozen in an air blast.

No difficulties were encountered in production by substitution of waxy rice flour for the wheat flour, and less lumping during cooking was found in the waxy rice batch than in the wheat batch. No flavor difference was found between the products. A sample of each product heated without stirring in a double boiler the day after processing showed the same appearance and liquid separation difference between the two à la king products that had been noted in laboratory tests of the sauce alone. The product containing waxy rice was completely smooth without stirring; that containing wheat flour had a slightly curdled or lumpy appearance that was not entirely eliminated even after stirring.

After 3 months of storage at 0° and 10° F. the thawed samples containing wheat flour had a stiff, rather flaky consistency resembling fish flakes. For the waxy rice flour samples those stored at 10° F. had a somewhat granular texture, while those stored at 0° had the same consistency as a sauce that had not been frozen. After heating in double boilers the sauces of both samples containing waxy rice flour were as smooth as before freezing; both samples containing wheat flour showed the typical somewhat uneven texture.

Consideration of results with respect to products other than sauces and gravies. Since instabilities such as lumping and liquid separation are defects that are frequently encountered in the food industry, the results obtained in this research have some implications that go beyond frozen sauces and gravies. Obviously, in any food where starch retrogradation during storage is a problem, the use of a suitable waxy cereal flour would be indicated if a short paste character is needed. On the other hand, if a long paste character is desired, presently available amylopectins would be more useful. It would be interesting to determine whether combinations of waxy cereal flours, waxy cereal starches and gelatin, for example, might give desserts and salad dressings that would be stable to freezing.

The incorporation of waxy flours or starches in thickened canned products that are subject to accidental freezing during shipment might make possible reclaiming of lots that are frozen. Since the reactions involved in liquid separation during freezing are apparently reversible even when waxy cereals compose only a portion of the thickening agent, it is conceivable that canned products containing these waxy cereals could be reclaimed after accidental freezing by mild heating of the cans.

The various changes such as increased thickening, gelation, curdling, and separation, that take place when thickened canned products are autoclaved and stored might be retarded by incorporation of waxy rice flour or starch in these products.

CONCLUSIONS

The type of thickening agent has been found to be a principal factor in the development of a curdled appearance and liquid separation in sauces and gravies subjected to freezing and frozen storage. The use of amylopectin starches and flours minimizes these defects, but since amylopectin starches, in contrast with some waxy cereal flours, have a long paste character, only certain flours appear suitable for use in sauces and gravies. Based on tests with the samples of waxy cereal flour available, waxy rice flour appears to be superior to waxy corn flour and waxy sorghum flour; if the appearance and liquid separation are important only in heated sauces and gravies, then the waxy white corn and rice flours are essentially interchangeable. After extensive storage waxy cereal flour sauces thawed at room temperature may show considerable liquid separation, but when the sauce is heated the liquid is taken up by the opaque phase.

The separation and curdled appearance of thawed sauces can be prevented for as long as 11 months at a storage temperature of 0° F. (—18° C.) by using waxy rice flour as the thickening agent. These defects can be considerably reduced for storage as long as 5 months at 0° F. (—18° C.) by using mixtures of wheat and waxy rice flours, particularly when the sauce is homogenized before freezing.

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[11] C. F. Van Valin Co., Snohomish, Washington.

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Temperatures Required by Fruits and Vegetables After Harvest[a]

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A REVIEW

Optimum temperatures for the transportation and storage of fruits and vegetables are discussed and the effects of other than optimum temperatures on the various fruits and vegetables are noted.

Transportation of fruits and vegetables from place of production to processing plant or wholesale market involves some risk. The shipment may be spoiled by growth of fungi or bacteria on the commodity or the fruit or vegetable may lose most of its desirable qualities because of physiological changes during transit.

DISEASE CONTROL

Control of rots may begin with selection of disease resistant varieties or strains and may be continued by protection of the crop with sprays and dusts while it is growing. After harvest, many diseases that attack growing plants do not develop further. Peach leaf curl, pear blight, and grape mildew are examples of such diseases. Others, however, cause serious damage to the commodity during shipping and marketing. Brown rot of peaches is an example of a disease that originates in the orchard and may cause further damage after harvest; orchard sprays are important in growing sound fruit free from infection. Many common rots of fruits and vegetables on the market are caused by fungi and bacteria that are of little importance in fields and orchards. Blue mold rot, gray mold rot, rhizopus soft rot, and bacterial soft rot are examples. Each of the fungi or bacteria causing rots has optimum temperatures for growth which in most cases lie in the range of 70° to 85° F. (21° to 29.5° C.). Some organisms can scarcely grow at all at 32° to 40° (0° to 4.5° C.) but others make headway at these temperatures. All fungi and bacteria grow more slowly at low temperatures than they do at the optimum range and even a 10° F. temperature reduction may decrease development by 50%.

A number of treatments have been developed for the control of decay during shipment. Some of these are borax washes for citrus fruits and sweet potatoes, hypochlorite and chloramine washes for citrus and certain other fruits and vegetables, Dowicide solutions for apples and pears, sulfur dioxide fumigations for grapes, copper-impregnated wraps for pears, and diphenyl-treated wraps and liners for citrus fruits. All should be considered only supplemental to adequate refrigeration.

PHYSIOLOGICAL CHANGES

Just as low temperature retards the growth of fungi and bacteria, both low forms of plant life, it slows down the life processes of fruits and vegetables, extending their life and preventing undesirable changes in flavor and physical condition. It is necessary to know the peculiarities of an individual fruit or vegetable, however, to use refrigeration most effectively for its preservation.

COLD-SUSCEPTIBLE FRUITS AND VEGETABLES

Let us consider first some fruits and vegetables that may be harmed by even moderately low temperatures.

Potatoes. Potatoes are a good example of a vegetable that is affected by low temperatures. It is generally known that potatoes become sweet if held at temperatures lower than 40° F. (4.5° C.) for a few weeks. Starch is converted to sugar within the tissues by enzymatic action and sugar slowly accumulates and imparts an undesirable sweet taste and a dark brown color to fried potatoes and potato chips. Manufacturers of potato chips know this and usually specify that shipments of potatoes should not be iced. In many cases chilled potatoes can be reconditioned by exposure to 70° to 80° F. (21° to 26.5° C.) for 1 to 4 weeks but varieties differ and some never recover their original quality, particularly if exposed to temperatures as low as 32° F. (0° C.). Another peculiarity of potatoes is that they can grow new skin-like tissue under injuries if temperatures are not too low and humidities are high enough. By this process injured areas on

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newly dug potatoes are healed. Healing is most rapid at temperatures of about 70° F. (21° C.) and high humidities. Wound periderm formation proceeds very slowly if at all at temperatures below 50° F. (10° C.).

Sweet potatoes. Sweet potatoes need a preliminary curing period at about 85° F. (29.5° C.) and a humidity of 85% to heal cuts and abrasions *(6)*. After this initial curing the best holding temperature is 55° F. (12.5° C.) *(1)*. At lower temperatures chilling injury takes place, causing darkening of the tissue, making the potatoes susceptible to certain rots and giving them poor culinary quality. Temperatures lower than 55° F. (12.5° C.) should be avoided during transit.

Tomatoes. Tomatoes if ripe may be held a few days at 32° F. (0° C.) but for keeping them a week or 10 days, 40° to 50° F. (4.5° to 10° C.) is preferable *(6)*. Most tomatoes to be shipped some distance are picked in the mature green or turning stage of maturity. The lowest temperature at which they should be held for more than a few days is 55° F. (12.5° C.), for they are susceptible to chilling injury. If held at 40° F. (4.5° C.) for more than 8 days they do not ripen satisfactorily and are susceptible to infection by certain rot organisms. At the other extreme, temperatures of 70° F. (21° C.) or slightly higher accelerate ripening and development of decays of the watery soft rot type, and at 80° F. (26.5° C.) or above good red color does not develop. The temperatures needed for transporting mature green tomatoes are 55° to 65° F. (12.5° to 18° C.).

Tomatoes grown in summer apparently have greater tolerance to low temperatures than fruit grown in the fall in cooler weather. This was demonstrated by Wardlaw *(7)* in Trinidad, where tomatoes grown in tropical weather could be held for 30 days at 41.5° F. (5.5° C.) without chilling injury. Kidd and West *(2)* in England found that the same was true for summer-grown hothouse tomatoes and that the fall-crop grown in cooler weather developed chilling injury in 10 days at 41° F. (5° C.).

Cucumbers, squashes, and melons. Cucumbers, squashes, and melons are susceptible to injury by temperatures that would be ideal for many fruits and vegetables in transit. Cucumbers develop pits and dark colored watery areas if held much more than 10 days at 45° F. (7° C.) or below. Chilling injury has been reported from as little as 2 days of exposure to 32° to 45° F. (0° to 7° C.) *(3)*. These damaged tissues soon become infected with decay organisms. Temperatures of 45° to 50° F. (7° to 10° C.) are recommended for cucumbers if they are to be in transit 10 days or longer. Exposures to 32° F. (0° C.) even for a week would not be harmful if the cucumbers could be used as soon as removed from low temperatures.

Squashes of the long keeping varieties such as Hubbard have the longest life at 50° to 55° F. (10° to 12.5° C.). They should be cured at 80° to 85° F. (26.5° to 29.5° C.) for about 2 weeks to ripen them and heal mechanical injuries before storage or long distance shipment.

Summer squashes keep best at 50° F. (10° C.). At 32° to 45° F. (0° to 7° C.) severe pitting develops in 8 days, and unless the squash is used immediately upon removal these pitted areas soon develop decay *(5)*.

Melons such as cantaloup, Honey Dew, Persian, and Casaba fail to ripen normally and become very susceptible to decay if held too long at low temperatures. One worker has reported that 4 days of exposure to 32° to 45° F. (0° to 7° C.) is long enough to cause slight injury and 8 days very definite injury *(4)*. Ripe melons are less susceptible to low temperatures than unripe melons. Commercial shipments of cantaloups are top-iced in spite of their known susceptibility to low temperatures, but only enough ice is used to cool the melons to about 40° F. (4.5° C.) and transit temperatures lower than 36° F. (2° C.) are seldom obtained. Honey Dew melons, which are more susceptible to chilling than cantaloups, have been injured by top-icing.

Other vegetables. Eggplant, okra, sweet peppers, and watermelons are other vegetables that show chilling injury.

Citrus fruits. Oranges, lemons, and grapefruit do not require low temperatures for their transport. Temperatures in the range of 40° to 45° F. (4.5° to 7° C.) are low enough for oranges and grapefruit and 45° to 50° F. (7° to 10° C.) is satisfactory for lemons. Grapefruit and lemons develop abnormalities of the flesh and skin if held several weeks at temperatures lower than 50° to 55° F. (10° to 12.5° C.). Oranges are less susceptible to chilling injury.

Other fruits. Cranberries and some varieties of apples, notably McIntosh, Rhode Island Greening and Yellow Newtown from unusually cool growing districts are injured by a month or longer storage at temperatures lower than 36° to 40° F. (2° to 4.5° C.), but these temperatures would be satisfactory for their transport.

Most subtropical fruits are susceptible to chilling injury. Although some of these fruits are not important to the processor, he may be interested to know that pineapples, bananas, mangoes, papayas, avocados, and olives are all injured by low temperatures in storage or transit. Each has its own particular requirement. Mature green pineapples should not be held at temperatures below 50° F. (10° C.), but fully ripe fruit can be held at 40° to 45° F. (4.5° to 7° C.) *(6)*. Bananas of the Gros Michel variety, the common variety imported to this country from Central America, are chilled by temperatures lower than 56° F. (13° C.) and remain in good condition longest at temperatures in the range of 56° to 60° F. (13° to 15.5° C.) *(6)*. The best temperatures for holding mangoes are 48° to 50° F. (9° to 10° C.), for papayas 45° F. (7° C.), and for avocados 40° to 45° F. (4.5° to 7° C.), the choice depending on variety *(7)*. Olives develop internal browning at temperatures lower than 45° to 50° F. (7° to 10° C.) and ripe olives are more susceptible than green ones *(6)*.

COLD TOLERANT FRUITS AND VEGETABLES

Many fruits keep their fresh quality longest if held at slightly above their freezing temperature, and the generally recommended storage temperatures are 31° to 32° F. (—0.5° to 0° C.) *(1)*. Apples, except for certain varieties, grapes and pears are stored at a degree or two lower temperature. Since the time in transit is usually 10 days or less, even for transcontinental trips, these low temperatures are not required and 36° to 40° F. (2° to 4.5° C.) has been satisfactory. Slow cooling of the fruit and exposure to warm temperatures during marketing can be much more damaging to the commodity than transit temperatures only 5° to 8° F. (—15° to —13° C.) above the ideal for long storage.

Some vegetables offer a different problem. Peas and sweet corn need the maximum of refrigeration to prevent loss of sugar and of desirable quality. For example, unrefrigerated sweet corn suffered a loss of 52% in sugar content in 24 hours following picking as compared with a 13% loss in corn that was iced within a few hours after picking *(8)* and held at 37° to 40° F. (3° to 4.5° C.) during shipment by placing ice between layers of sacks in the truck. Quick cooling to about 33° to 35° F. (0.5° to 1.5° C.) and holding at these temperatures or only a few degrees higher would be ideal for vegetables that lose edible quality as fast as do corn, peas, green lima beans, broccoli, and asparagus. Leafy vegetables such as spinach and other greens, carrots, beets, and lettuce also require quick cooling to temperatures of about 35° to 36° F. (1.5° to 2° C.) and transit temperatures of 32° to 36° F. (0° to 2° C.) to prevent decay. Hydrocooling or package icing and body icing of the load are the refrigeration methods commonly used to provide the low temperatures needed by these vegetables.

String beans are best handled at temperatures in the range of 32° to 40° F. (0° to 4.5° C.) but they are not usually wet by hydrocooling or top icing. Celery likewise needs similar low temperatures and is often hydrocooled and top-iced. Cabbage and cauliflower require

temperatures of 40° F. (4.5° C.) or less and top-icing the car after loading is the common practice. Onions, if well cured, offer no particular problem in shipping. They should be kept as dry as possible with good air circulation and air temperatures of 32° to 40° F. (0° to 4.5° C.).

SUMMARY

The problems of fruit and vegetable transport include the risks of microbiological spoilage and of undesirable physiological changes in the commodity. Maintaining the correct temperature environment during transport offers the best solution for preventing spoilage and loss of desirable qualities. Fruits and vegetables differ in their temperature requirements. Those that are susceptible to low temperature injury are potatoes, sweet potatoes, tomatoes, cucumbers, squashes, melons, eggplant, okra, sweet peppers, some varieties of apples, cranberries, pineapples, bananas, mangoes, papayas, avocados, and olives. Some of these commodities require intermediate transit temperatures and avoidance of temperatures below 40° F. (4.5° C.) for some and below 55° F. (12.5° C.) for others. Most of the hardy fruits such as apples, pears, grapes, cherries, plums, peaches and berries keep best when stored close to their freezing temperature and temperatures of 31° to 32° F. (0.5° to 0° C.) or a degree or two lower are generally recommended for long storage, but for the week or 10 day transit period 36° to 40° F. (2° to 4.5° C.) is satisfactory. Vegetables that lose quality quickly such as peas, sweet corn, green lima beans, broccoli, and asparagus should be cooled promptly to 33° to 35° F. (0.5° to 1.5° C.) and held at these temperatures in transit. Spinach, greens, lettuce, carrots, beets, celery, cauliflower, and cabbage need similar temperatures because of their susceptibility to decay. Hydrocooling or package icing and top icing the load are common practice for these vegetables.

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Retardation of Rancidity in Pecans

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Experimental results are reported on the development of rancidity in pecans which were stored under varying conditions of controlled temperature and humidity. Storage tests were also conducted with pecans which had been coated with various antioxidants in a sucrose syrup base. Pecans of good quality were found to resist rapid changes of rancidity development and this resistance was further augmented by coating the nutmeats with a 40% sucrose syrup base. The progress of rancidity development, the effect of moisture loss, the effect of temperature, and the absorption of foreign odors by these nutmeats are also discussed.

The development of rancidity in pecans is a major form of their deterioration and its prevention or at least retardation is of interest to industries using these nut meats.

Most of the investigations concerning the development of rancidity in pecans have had to do with controlled storage tests. Blackmon *(3)* experimented with the cold storage of pecans and found that the nuts could be kept fresh from one season to the next when stored at 32° F. (0° C.), provided they were placed in storage soon after harvest when thoroughly dry and before the oil had begun to break out. Brison *(4)* reported similar results and found that kernels which had been stored at 5° F. (—15° C.) were suitable for marketing throughout a period of two years. He also emphasized that the pecans should be stored soon after harvest while fresh and before any chemical changes had taken place which could cause rancidity. Wright *(15)* stored unshelled pecans at 32° F. (0° C.) and 75% relative humidity, and reported the nuts to be in good condition for more than a year after harvest. At 50° F. (10° C.) storage, the nuts remained good for about six months, but at 70° F. (21° C.) they became stale to rancid in three months. When packed in vacuum, these kernels kept for two to three years at 32° F. (0° C.) and 50° F. (10° C.) but only six to eight months at 70° F. (21° C.). Abbott *(1)* found that the development of rancidity in shelled pecans could be arrested or partially prevented by replacing the air in the jars in which they were packed with nitrogen, hydrogen, or evacuating the jars to a 25 inch vacuum. Replacement of the air with carbon dioxide did not prevent the development of rancidity. When coated with collodion or water glass, the unshelled nuts became rancid as quickly as did untreated nuts.

It appears that the development of rancidity in pecans can be retarded for at least one year by following adequate measures of cold storage soon after the nuts are harvested. The use of low storage temperatures necessitates providing properly constructed containers so that the nuts are not subjected to the presence of any odoriferous foods or humidity conditions which would cause their moisture content to either increase or decrease appreciably. Development of rancidity may also be slowed down by packaging the nut meats in hermetically sealed vacuum cans. However, these methods of control are impractical for application to baked goods containing pecans and having an extended shelf life.

Within recent years there has been a considerable amount of research in the use of antioxidants for the prevention of rancidity in fats, oils, and various fatty footstuffs. Many investigators as Lunberg, Halvorson, and Burr *(7)*; Riemenschneider, Herb, Hammaker, and Luddy *(11)*; Riemenschneider and Speck *(12)*; Silver *(13)*; Smith, Brady, and Comstock *(14)*; Pearl and McCoy *(9)*; and others have studied the effects of various antioxidants in stabilizing lards, fatty fish, bacon, and other fatty substances. Much of their interest has centered around the antioxygenic properties of nordihydroguaiaretic acid (NDGA) and this same antioxidant used in combination with several synergists.

The use of antioxidants for delaying rancidity in nut meats has not received much attention. Reznikova *(10)* reported the keeping-time of nut meats (peanuts and walnuts) to be prolonged when packed in oatmeal. The use of antioxidants and synergists such as glycine, alanine, tartaric, citric, lactic, maleic, and phosphoric acids, pyrogallol, hydroquinone, naphthol, orcin with phosphoric acid, lactose, maltose, levulose, dextrose, chestnut meal, and oatmeal water, showed some slight antioxygenic properties when used with the above nut meats but were of no practical benefit. Cruess and Armstrong *(5)* also reported some success in delaying rancidity development in walnuts by incorporating various antioxygenic agents in syrups and sugar coatings.

From year to year we have noticed inconsistencies in the quality of pecans. Occasionally slightly rancid shipments were received and frequently the appearance, texture, and flavor of the kernels varied within the same shipment. Storage tests performed with representative samples of shipments showed a lack of uniformity in that some pecans became rancid quicker than others. This lack of uniformity has, in some instances, contributed to decreasing the shelf life of a pecan containing product such as fruit cake. There is also the problem of slight incipient rancidity being in progress at the time the nut meats are received. This change may not be advanced far enough at the time to be noticed organoleptically, however, later during the shelf life of the baked fruit cake product rancidity develops in these pecans to the point of becoming organoleptically noticeable. We are aware that in years of heavy pecan production it is often necessary for the processor to carry over the surplus crop until the following year when, owing to a lighter crop for that year, better prices will possibly prevail. Consequently, the methods of storing and handling the carry-over surplus will have a decided effect on the quality of these pecans and their stability when finally in the hands of bakers, confectioners, and ice cream manufacturers. In general, fresh pecans are fairly stable nut meats and resist rapid changes of rancidification. Bailey *(2)* reports refined pecan oil to contain 0.45% tocopherols. The nut meats therefore, possess, to some degree, natural means of delaying the development of rancidity.

In this report references to the rancidity of pecans have been based upon organoleptic tests. Several investigators as Brison *(4)*, Dustman *(6)*, and Wright *(15)* found that the Kreis test on many occasions did not give an accurate indication of rancidity in extracted pecan and walnut oils. As later shown in this report, we were not able to apply the Kreis test as a criterion for detecting rancidity in pecan oils. Brison *(4)* also found that the free fatty acid content could not be used as a test for rancid pecan oils. McGlamery and Hood *(8)*, however, reported rancidity development in pecans by Kreis valves and peroxide numbers but noted significant differences by organoleptic flavor scores before being detected by these chemical tests.

Several factors of the rancidity problem of pecans were of interest to us. Most important of the considerations was the progress of rancidity in commercial shelled pecans when held under varying storage conditions. Also of interest was the application of the Kreis test for rancidity with extracted pecan oils, the effect of various antioxygenic substances in delaying rancidity development in pecans, the absorption of flavors by pecans, and the stability of the nut meats during the shelf life of fruit cake.

EXPERIMENTAL PROCEDURE AND RESULTS

In most of the experimental tests, commercial pecans from regular marketing channels were used. Hereafter these will be referred to as Type A pecans. In a few tests fresh unshelled pecans were acquired and used for comparison. These nut meats were held in the unshelled condition at 35° F. (1.5° C.) and shelled as needed. For reason of simplicity these pecans from unshelled stock will be referred to as Type B pecans.

Type A pecan halves were stored at room temperature 75-80° F. (24-26.5° C.), refrigeration temperature 35-40° F. (1.5-4.5° C.), and at 96-98.6° F. (35.5-37° C.) with relative humidities, in the latter case, of approximately 50%. With one exception, the pecans were packaged in small cardboard boxes and wrapped with cellophane. A few modifications with some samples were added, such as spraying the pecans with 0.1% aqueous ascorbic acid prior to storage, and holding the samples at 150° F. (65.5° C.) for one hour before storage.

The results as indicated in Table 1 showed that rancidity progressed more rapidly at elevated storage temperatures of 96-98.6° F. (35.5-37° C.). The initial changes noticed were loss of flavor and dryness. The addition of 0.1% aqueous ascorbic acid by spray appeared to have a beneficial effect during early storage (first month). Samples stored at 35-40° F. (1.5-4.5° C.) were of good quality following five months of storage. The Kreis test for rancidity with the extracted pecan oils (oils were expressed by use of a Carver Press and centrifuged to clarify) did not show any correlation with organoleptic rancidity. Pecan oils, which varied from slightly rancid to rancid taste, gave negative Kreis tests. One sample of pecan oil which had a very strong rancid taste gave a very weak Kreis reaction.

TABLE 1

Effect of temperature on the storage of Type A [a] shelled pecans

Container	Treatment	Storage temperature, ° C.	Condition after storage for									Kreis [b] test
			1 month			3 months			5 months			
			Color	Texture	Flavor	Color	Texture	Flavor	Color	Texture	Flavor	
Cardboard-cellophane wrapped	None	1.5 to 4.5	.....	.....	.....	.....	.....	.....	bright	good	excellent	negative
		24 to 26.5	.....	.....	.....	.....	.....	.....	dark	brittle	rancid	negative
		35 to 37	sl. dark	brittle	stale	dark	brittle	rancid	.....	.....	.....	negative
Cardboard-cellophane wrapped	Sprayed with 0.1% ascorbic acid	1.5 to 4.5	.....	.....	.....	.....	.....	.....	bright	good	excellent	negative
		24 to 26.5	.....	.....	.....	.....	.....	.....	dark	brittle	rancid	negative
		35 to 37	bright	fair	fair	dark	brittle	sl. rancid	.....	.....	.....	negative
Cardboard-cellophane wrapped	Held at 65.5° C. for 1 hr. before storage	1.5 to 4.5	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
		24 to 26.5	.....	.....	.....	.....	.....	.....	dark	brittle	rancid	negative
		35 to 37	sl. dark	brittle	stale	dark	brittle	rancid	.....	.....	.....	negative
Cardboard box, not wrapped	None	35 to 37 (R. H. 50%)	dark	brittle	rancid	very dark	brittle	strongly rancid	.....	.....	.....	trace

[a] Type A—Commercial shelled pecans from regular marketing channels.
[b] Kreis test performed at end of respective storage periods.

TABLE 2

Oxidation of oil from Type A [c] shelled pecans

	Hours exposed on Swift Stability Apparatus, air flow 2.33 cc./sec., bath temp. 98° C.							
	0 (fresh)	1	4	5	17	24	36	48
Flavor and aroma	good	good	good	good	sl. bland	bland	bland	sl. rancid
Color	light amber	no change	no change	no change	very light amber	nearly colorless	nearly colorless	nearly colorless
Kreis test	negative	negative	mild reaction	mild reaction	strong reaction	intense reaction	intense reaction	intense reaction

[c] Type A—Commercial shelled pecans from regular marketing channels.

The Kreis test was also utilized on fresh pecan oil from Type A pecans which had been run on the Swift Stability Apparatus for increasing periods of time. A mild Kreis reaction (see Table 2) was noted after the oil had been oxidized for 4 hours. However, the oil still had a pleasing odor and taste free of rancidity. After running the oil for 17 hours on the Stability Apparatus, no rancid taste or odor was noticeable but an intense positive Kreis test was obtained.

In attempts to accelerate rancidity development in pecans, two series of Type B pecan halves were stored in sealed glass jars at 122-124° F. (50-51° C.) for 37 days. One series of the nut meats was stored with small vials containing calcium chloride inside the jars while the other series did not contain the calcium chloride vials. The progress of rancidity was slightly more rapid with the samples containing the calcium chloride vials. The 6 day samples showed dryness and flavor loss. Samples from this same series were noticeably rancid after 23 days of storage while those stored without calcium chloride vials did not become organoleptically rancid until after 27 days of storage. Before storage, the pecans had a moisture content of 3.21%. After 37 days of storage, when both series showed decided rancidity, the samples containing calcium chloride vials had a moisture content of 1.67% while those not containing calcium chloride vials contained 2.53% moisture. See Table 3 for results.

A series of experiments was conducted in which Type A pecans were treated with antioxygenic agents and stored at 113-114.8° F. (45-46° C.); room temperature, 75-80° F. (24-26.5° C.); and controlled temperature-humidity conditions of 90° F. (32° C.) and 85% relative humidity. The latter temperature-humidity conditions involved only a few of the test samples.

For comparison Type B pecans were shelled and also treated with various antioxygenic agents. These pecans, however, were

TABLE 3

Effect of moisture loss on the acceleration of pecan rancidity [d]

Container	Storage temp., ° C.	Condition after storage for			
		6 days	23 days	27 days	37 days
Sealed glass jars	50-51	sl. dryness, flavor loss	dark, brittle, and stale	slightly rancid	very rancid moist.: 2.53% [e]
Sealed glass jars with calcium chloride vials	50-51	dry with flavor loss	dark, brittle, and rancid	very rancid	very rancid moist.: 1.67% [e]

[d] Type B—From fresh unshelled pecans stored at 1.5° C.
[e] Original moisture: 3.21%.

stored only at 113-114.8° F. (45-46° C.). The antioxidant and synergist components were, in the majority of cases, incorporated in water containing 40% sucrose with 2% of Tween 20 [f] added as a dispersing agent. Some preparations were made without the 40% sugar added and with or without the Tween 20. The nuts were dipped for one minute, drained, dried in an air convection oven at 122° F. (50° C.) for one hour, and then packaged in small cellophane bags prior to storage.

The results of these tests are shown in detail in Table 4. Since varying the concentration of the antioxidants had so little effect within each test series, the results as recorded apply to all concentrations unless noted otherwise. With both the Type A and Type B pecans the use of 40% sucrose syrup alone demonstrated better antioxygenic properties in most cases and the incorporation of various additional antioxidants in this syrup base failed to increase this activity. The pecans treated with NDGA in a water and Tween 20 base became rancid quicker than when the 40% sucrose syrup was added. In all cases the nut meats became rancid at a faster rate when stored at the higher temperature of 113-114.8° F. (45-46° C.). The stor-

[f] Tween 20 (polyoxyethylene sorbitan monolaurate) is manufactured by the Atlas Powder Co., Wilmington, Del.

TABLE 4

Effect of antioxidants with or without synergists on the storage of Type A (commercial) and Type B (fresh) pecans

Treatment	Type of pecans used	Storage Temp. °C.	Condition after storage for							
			2 weeks	4 weeks	6 weeks	8 weeks	10 weeks	12 weeks	16 weeks	24 weeks
			Flavor and/or texture	Flavor and/or texture	Flavor and/or texture	Flavor and/or texture	Flavor and/or texture	Flavor and/or texture	Flavor and/or texture	Flavor and/or texture
None	Commercial	45-46	sl. rancid and brittle	rancid	very rancid	.....	.....	.....	.....	.....
		24-26.5	.....	.....	.....	.....	.....	stale to sl. rancid	rancid	very rancid
		32 (85% R.H.)	good	.....	fair to good flavor, fair texture	.....	stale and rubbery	"off" flavor	.....	.....
	Fresh	45-46	.....	.....	.....	.....	stale and brittle	stale to sl. rancid	rancid	very rancid
Heated 1 hr. at 50° C.	Commercial	45-46	stale and brittle	rancid	very rancid	.....	.....	.....	.....	.....
		24-26.5	.....	.....	.....	.....	.....	stale to sl. rancid	rancid	very rancid
	Fresh	45-46	.....	.....	.....	.....	stale and brittle	stale to sl. rancid	rancid	very rancid
Water-dipped	Commercial	45-46	sl. stale and brittle	sl. rancid	rancid	very rancid	.....	.....	.....	.....
		24-26.5	.....	.....	.....	.....	.....	stale to sl. rancid	rancid	very rancid
	Fresh	45-46	.....	.....	.....	.....	stale and brittle	stale to sl. rancid	rancid	very rancid
Dipped in 2% "Tween 20," aqueous dispersion	Commercial	45-46	fair	stale, "off" flavor [h]	sl. rancid	rancid	very rancid	.....	.....	.....
		24-26.5	.....	.....	.....	.....	.....	.....	stale to sl. rancid	rancid
	Fresh	45-46	.....	.....	.....	.....	.....	stale and brittle	stale to sl. rancid	rancid
Dipped in 40% sucrose syrup	Commercial	45-46	fair to good	fair	stale and brittle	stale to sl. rancid	rancid	.....	.....	.....
		24-26.5	.....	.....	.....	.....	.....	.....	stale	sl. rancid
		32 (85% R.H.)	.....	very good	.....	good	.....	.....	good flavor, fair texture	stale and rubbery
	Fresh	45-46	.....	.....	.....	.....	.....	stale and brittle	stale to sl. rancid	rancid
40% Sucrose syrup plus 2% "Tween 20" (base dip) [g]	Commercial	45-46	fair to good	fair, sl. "off" flavor [h]	stale and brittle	stale to sl. rancid	rancid	.....	.....	.....
		24-26.5	.....	.....	.....	.....	.....	.....	stale	sl. rancid
	Fresh	45-46	.....	.....	.....	.....	.....	stale and brittle	sl. "off" flavor [h]	sl. rancid
Base dip [g] with 0.10, 0.05, and 0.01% NDGA	Commercial	45-46	fair, bitter taste [i]	stale	stale to sl. rancid	rancid	very rancid	.....	.....	.....
		24-26.5	.....	.....	.....	.....	.....	.....	stale, bitter [i]	sl. rancid
	Fresh	45-46	.....	.....	.....	.....	.....	stale, bitter [i]	sl. rancid	rancid
Base dip [g] with 0.10, 0.05, and 0.01% NDGA and 0.010, 0.05, and 0.01% alpha tocopherol	Commercial	45-46	fair, bitter taste [i]	stale	stale to sl. rancid	rancid	very rancid	.....	.....	.....
		24-26.5	.....	.....	.....	.....	.....	.....	stale, bitter [i]	sl. rancid
	Fresh	45-46	.....	.....	.....	.....	.....	stale and brittle	stale, sl. bitter [i]	sl. rancid
Base dip [g] with 0.10, 0.05, and 0.01% NDGA and 0.10, 0.05, and 0.01% ascorbic acid	Commercial	45-46	fair to good	fair	stale and brittle	stale, sl. bitter [i]	rancid	.....	.....	.....
		24-26.5	.....	.....	.....	.....	.....	.....	stale, sl. bitter [i]	sl. rancid
		32 (85% R.H.)	.....	sl. bitter [i]	.....	bitter, [i] rubbery	.....	.....	stale	sl. rancid
	Fresh	45-46	.....	.....	.....	.....	.....	stale, sl. bitter [i]	.....	sl. rancid
Base dip [g] with 0.25, 0.15, and 0.05% mixed alpha, beta, and gamma tocopherols	Commercial	45-46	fair	stale	sl. rancid	rancid	very rancid	.....	.....	.....
		24-26.5	.....	.....	.....	.....	.....	.....	stale and brittle	sl. rancid
Base dip [g] with 0.25, 0.15, and 0.05% Griffith's G-4 antioxidant [j]	Commercial	45-46	fair	stale	sl. rancid	rancid	very rancid	.....	.....	.....
		24-26.5	.....	.....	.....	.....	.....	.....	stale and brittle	sl. rancid
	Fresh	45-46	.....	.....	.....	.....	.....	stale and brittle	sl. rancid	rancid
Dipped in water containing 2% "Tween 20" and 0.10, 0.05, and 0.01% NDGA	Commercial	45-46	bitter [i]	rancid	very rancid	.....	.....	.....	.....	.....
		24-26.5	.....	.....	.....	.....	.....	.....	stale, bitter [i]	rancid
Sprayed with crude vitamin E concentrate and blotted dry	Commercial	45-46	very rancid after 1 week [k]	.....	.....	.....	.....	.....	.....	.....

[g] Base dip: 40% sucrose and 2% "Tween 20" in water.
[h] Off flavor contributed by "Tween 20."
[i] Bitter taste contributed by NDGA (nordihydroguaiaretic acid) at 0.10% concentration.
[j] Contained corn oil, lecithin, propyl gallate, and citric acid. The Griffith Labs., Chicago, Ill.
[k] Crude vitamin E concentrate imparted rancid odor and taste to pecans.

age temperature of 90° F. (32° C.) and controlled humidity of 85% delayed the development of rancidity but eventually the pecans became spongy and rubbery from adsorption of additional moisture. A contributory "off" flavor was noticed from the use of Tween 20 and a bitter flavor was imparted by NDGA which was most noticeable when the 40% sucrose syrup was omitted. There was a decided difference in the rate of rancidity development betwen the Type A and Type B pecans stored at 113-114.8° F. (45-46° C.). The Type A pecans became rancid approximately four times as fast as Type B pecans. The crude vitamin E concentrate used as a spray imparted a very rancid odor and flavor to the nut meats within a week when stored at 113-114.8° F. (45-46° C.). This same strong rancid odor was imparted to parchment paper containing the vitamin concentrate and stored for one week at 113° F. (45° C.).

Some additional tests were performed to investigate other factors that might change the flavor of pecans. It had been noticed occasionally that nut meats, especially pecans, which were stored at 35-40° F. (1.5-4.5° C.) in unsealed containers in the presence of odoriferous foods, absorbed their odors and changed in flavor. Brison *(4)* found that pecans stored in cloth bags for eleven months at 32° F. in the presence of smoked meat picked up a taste judged as "strong," "rancid," and "stale." Our storage tests involved storing pecan kernels in sealed glass jars along with small open vials containing flavors that are used extensively in bakery products. The flavors used were butter, madeira, vanilla, lemon, and orange and the storage temperatures were 35° F. (1.5° C.) and 75-80° F. (24-26.5° C.) for one month. The results are shown in Table 5. At both

TABLE 5

Absorption of flavors by pecans during storage

Type of flavor [1]	Effect on pecans after storage of one month at	
	1.5° C.	24°-26.5° C.
Lemon (oil and water emulsion)	very slight lemon taste in pecans	sl. lemon taste in pecans
Orange (oil and water emulsion)	orange flavor hardly detected	sl. orange taste in pecans
Vanilla (vanillin and coumarin blend in alcohol)	sl. vanilla taste in pecans	fairly strong vanilla taste in pecans
Madeira (oil and water emulsion)	objectionable strong taste	objectionable strong taste
Butter (butyric acid blends)	objectionable strong taste	objectionable strong taste

[1] Open vials containing flavors placed in sealed jars with pecans.

storage temperatures two of the flavors, madeira and butter, noticeably affected the flavor of the pecans. The nuts had a very disagreeable taste and possibly could be judged as "rancid" by persons not accustomed to true pecan rancidity. The vanilla flavor was easily detected in the sample stored at 75-80° F. (24-26.5° C.) but was hardly noticeable in the one stored at 35° F. (1.5° C.). The lemon and orange flavors had very little effect on the pecans during one month of storage at the above temperatures.

Additional tests were made using fruit cakes baked with and without rum and butter flavors and with the two in combination. These samples were stored at 75-80° F. (24-26.5° C.) for a period of six months. No dissimilarity was detected in the pecans on and in the fruit cakes baked with and without the test flavors. As the storage time progressed, none of the pecans retained their original taste but, instead, seemed to contain a somewhat composite taste of the fruit cakes themselves. Rancidification of the nut meats was not organoleptically evident and any slight rancidity which may have been present was masked by the fruit cake taste in the nuts. Control samples of the pecans used in preparing the fruit cakes were packaged in cellophane bags with an outer wrapping of pliofilm and stored along with the cakes at 75-80° F. (24-26.5° C.) After six months of storage these nuts had partially dried out, lost flavor, and were slightly rancid.

DISCUSSION

These experimental results show that pecans, which are fresh and of good quality, are stable and resist rapid development of rancidity. Rancidification of pecans is accelerated as the storage temperature is increased and humidity remains low. Pecan nut meats which had been properly packaged [m] and stored at 75-80° F. (24-26.5° C.) remained edible, that is retained their desirable flavor and texture for about a month. Continued storage caused these nut meats to gradually dry out and become brittle, lose flavor, and eventually darken and take on a strong rancid taste. Pecans which were treated so as to lose moisture more rapidly also became rancid at a faster rate. It would appear that the acceleration of rancid development in pecans at higher storage temperatures, that is, 96-98.6° F. (35.5-37° C.), 113-114.8° F. (45-46° C.), and 122-124° F. (50-51° C.) was due, in part, to a faster drying-out of the nut meats. The storage tests conducted by Brison *(4)* showed a correlation between moisture loss and rancidity development. However, McGlamery and Hood *(8)* in their experiments with heat-treated pecans stated that the reduction in moisture content of these treated nut meats may have contributed to retarding their development of rancidity.

At a storage temperature of 90° F. (32° C.) rancidity was delayed when the relative humidity was controlled at 85%. Under these storage conditions flavor retention also was obtained for six weeks or slightly longer with untreated pecans. Continued storage beyond 6 weeks resulted in deterioration in texture (rubbery texture) along with the development of an "off" [n] flavor other than that of true pecan rancidity. Similarly stored nut meats with a 40% sucrose syrup coating remained edible after 16 weeks of storage.

All references to rancidity were dependent entirely upon organoleptic tests. The Kreis test was unsatisfactory since it gave no correlation with the degree of rancidity as indicated by taste and smell. Additional chemical tests were not attempted inasmuch as failure to report rancidity by such analyses had been reported by other investigators.

[m] Packaged in moisture-proof cellophane bags or cellophane wrapped cardboard boxes.

[n] A ketonic flavor suggestive of microbiological enzymatic activity.

The use of antioxygenic agents for delaying rancidity development in Type A pecans was partially successful but of questionable value from a practical standpoint. In all the accelerated tests conducted at 113-114.8° F. (45-46° C.), the treated samples became rancid at a slower rate than those pecan samples which were not treated. The bitterness contributed by NDGA was undesirable and nullified the efficacy of any rancidity delaying properties of the antioxidant. The use of a coating containing 40% sucrose syrup provided the best means of delaying rancidity in the accelerated storage tests with pecans and did not contribute any bitter or "off-taste" to the nut meats. A slight sweetness was added to the pecans but this characteristic was not an undesirable one. It is believed that the 40% sucrose syrup acted both as a protective coating and synergist. Its influence in delaying rancidity was not extended by the additional incorporation of antioxidants in the syrup.

The initial quality of pecans undergoing storage tests is of greatest importance. This factor is readily noticeable when comparing the progress of rancidity development at 113-114.8° F. (45-46° C.) between the shelled Type A pecans and those from the Type B stock. Although the Type A pecans were originally satisfactory, they obviously were not as stable or rancid-resistant as those taken from the Type B stock. With the fresh Type B pecans, the use of antioxygenic agents was of less value or significance.

Foreign odors are absorbed by pecans. Although the volatility of some flavors is considerably lower at refrigeration temperature, it is possible for the nuts to absorb these odors during extended periods of refrigerated storage and eventually alter their flavor. Consequently it is very important that pecans be stored either in sealed containers or apart from any other odoriferous substances. It is equally important that the nut meats be packaged in odorless containers which are free of any greased liner coatings that could become rancid during prolonged storage.

During storage of fruit cakes, the pecans of good quality lose their characteristic taste and gradually take on the general flavor of the cake. The major changes noticed in nut meats on and in fruit cakes were due to increase in moisture content and the absorption of flavors from other cake ingredients and not to rancidity development.

In the introduction of this report, mention was made of pecans becoming rancid on and in stored fruit cake. It is now apparent that in such instances the pecans are of inferior quality and in the incipient stage of rancidity when used. This condition becomes more pronounced upon storage. Usually the fruit cake taste imparted to pecans is strong enough to mask any slight traces of rancidity.

SUMMARY

Fresh pecans of good quality resist rapid changes of rancidity development at ordinary room temperatures. Rancidity development is slow and was shown to be accelerated by storing the nut meats at elevated temperatures in the range of 96-124° F. (35.5-51° C.). As the pecans dry out at these elevated storage temperatures, loss of flavor, darkening, and brittleness are the first noticeable defects; they are later followed by increasing development in rancid odor and taste.

Freshness can be retained in high quality pecans stored at ordinary room temperature (preferably in the dark) for a month to 6 weeks by packaging the nut meats in moisture-proof cellophane bags. For longer storage of the pecans, low temperature storage, that is, 35° F. (1.5° C.) or less should be resorted to for preserving freshness.

Pecans which were well packaged in moisture-proof cellophane bags and stored in a cabinet held at 90° F. (32° C.) and 85% relative humidity retained good flavor and fair texture for 6 weeks. The addition of a 40% sucrose syrup coating prolonged the keeping-time of the pecans, under this type of storage, to 4 months. The incorporation of various antioxidants in the syrup did not improve its antioxygenic properties. Nordihydroguaiaretic acid (NDGA) dispersed with 2% Tween 20 in a water dip did not delay rancidity development in pecans. The NDGA when used in higher concentrations (0.10%) contributed a bitter taste to the nut meats.

Pecans readily absorb foreign and undesirable odors. It is important that the nut meats be stored in places away from such odors or in odorless seal-proof containers free from liner coatings that can become rancid.

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Book Review

VOM KORN ZUM BROT. By Elisabeth Tornow, 265 pp., 48 illustrations. Theodor Steinkopff, Dresden and Leipzig, Germany, 1950. Price paper cover 10 RM; bound 11.50 RM.

As the title implies, this book deals with grains and grain processing from the field to the baked products. It does so in an extensive rather than an intensive manner. It includes cereal chemistry, plant pathology, entomology, and bacteriology as well as milling and baking technology. Six main divisions cover grain, grain pests, milling, flour, baking adjuncts, and baked products. Three hundred ninety-four literature references are cited in footnotes; these are predominantly to German, Russian, and French journals and patents; very few British and American references are given.

The breadth of subjct matter makes the book of interest to one looking for a description of European milling and baking practices. Much historical information is included. It is likely that the specialist in a particular field of cereal technology will find its greatest value in acquainting him with topics outside his own specialty. American practices are mentioned in some places. Erroneous statements are made in connection with some of these. For example, it is said that enrichment is practised in the United States because bleaching destroys vitamins. An inaccurate description of "Brown 'N' Serve" rolls apparently results from a confusion between the Fahrenheit and Centigrade temperature scales.

The book is of a convenient size, has a good table of contents, and is well indexed. Quality of the paper, binding, and illustrations is only fair.

P. E. RAMSTAD.

THE CHEMISTRY AND TECHNOLOGY OF WINES AND LIQUORS. By Karl M. Herstein and Morris B. Jacobs. Second edition, pp. 430 plus index, 60 tables, and 59 figures. D. Van Nostrand Co., Inc., New York, N. Y., 1948. Price $7.50.

As the previous (1935) edition of this book, this is a general survey of a greatly diversified field. A great deal of information has been brought together in this volume. The first four chapters deal with theoretical considerations followed by a 26 page discussion of yeasts and other microorganisms. The subsequent chapters discuss malt, distillation, whiskey manufacture, aging and blending, brandy, rum, gin and other distilled liquors, wine, and liqueurs and cordials. The following two chapters, dealing with the analyses of various products, consist mostly of tables of analyses, government definitions and analytical methods, the latter reprinted from the A.O.A.C. Official and Tentative Methods of Analyses.

This is an excellent volume to turn to for general information on any of the products listed above, but of necessity the discussions will be of little aid to anyone interested in manufacturing details and engineering construction. It would seem that while there was a definite need for such discussions at the end of the prohibition period, both the technical literature and the general knowledge of the public concerning alcoholic beverages has come a long way since that time. In this connection the lack of literature references is most unfortunate. For instance, the chapter on wines (36 pages) has five (5) references and only two of these deal specifically with wines. The very good chapter on liqueurs and cordials (34 pages) contains even fewer references. This certainly gives little opportunity to the interested reader to search for further information. The presentation is straight-forward and the arrangements and printing are excellent. The many flow sheets and diagrams on production methods are particularly helpful.

This book will be very useful to those who seek an overall picture of the alcoholic beverage industry.

Z. I. KERTESZ.

THE LOW FAT, LOW CHOLESTEROL DIET. By E. Virginia Dobbin, Helen G. Gofman, Helen C. Jones, Lenore Lyon and Clara-Beth Young. pp. 352 plus index. Doubleday and Company, Inc., Garden City, N. Y., 1951. Price $3.45.

Twenty or even ten years ago there would have been little justification in calling a book of such nature to the attention of food technologists. However, by now the preparation of specific therapeutic foods, of common food products prepared without certain ingredients as table salt or sugar has become a lively even if as yet small branch of the food industries. The present volume opens up further possibilities for such products.

Without entering the discussion of the relationship between cholesterol and various cardiovascular ailments we may state bluntly that the existence of a close relationship is now widely accepted. Thus the need for low-fat, cholesterol-free diets arises. While attempts have been made in the past to describe the preparation of such foods, this is the first comprehensive book on low-fat, cholesterol-free diet.

This volume is much more than a cook book. The organization is excellent and the analytical evaluation of the prepared dishes for their fat, cholesterol, protein and carbohydrate contents and calculated calorie contents is clearly presented. After a discussion of cholesterol and fat, several chapters deal with the general subject of special foods. This is followed by a long list of recipes which are noteworthy for the attention given to flavor, flavorings and variety. Then menus are given and finally, in the appendix, extensive tables on the fat and cholesterol content of various foods followed by some more general discussion of nutritional practices.

Food processors interested in the development of special food products might well study this book in an attempt to develop new items for the market. The manufacture of such food products seems to be rewarding and might be even more so as the application of special diets becomes more common.

Z. I. KERTESZ.